THE REACTIONS OF ALKYL RADICALS FROM ALDEHYDES

BY

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ABSTRACT OF THESIS

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The study of the photo-initiated chain decomposition of aldehydes has been extended to include isovaleraldehyde, and the reactions of isobutyl from this source have been studied. Isobutyl is compared with other alkyl radicals.

A determination of the absolute rate constant of isopropyl combination has been made using the intermittent illumination photolysis of isobutyraldehyde. Ethylene was added as a marker, the rate of addition of isopropyl to the double bond was used as a measure of relative radical concentration. A first-order termination correction was applied when deriving the combination rate constant.

The photolytic radical sources available for absolute rate determinations by the intermittent illumination method have been compared, and the absolute rate constants for alkyl radical combinations have been compared with collision rates.

Some work on the photolysis of ketones inhibited by nitric oxide and oxygen is also included.

Use other side if necessary.

TO MY PARENTS

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Eileen L. Metcalfe.

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PREFACE

Chapter I consists of a survey of the field of alkyl radical reactions, including the results of the work on the isobutyl radical, presented in Chapter III of this thesis. Therefore it may be considered as a combined Introduction and Discussion of isobutyl. This is followed by a chapter on the general experimental technique, then chapters on the experimental results for isobutyl, isopropyl combination, and inhibition in ketone photolyses. Chapter VI is a discussion of the work on the absolute rate of isopropyl combination.

TABLE OF NOMENCLATURE

A	=	A factor } Arrhenius parameters.
E	=	Activation energy } Arrhenius parameters.
$D(Y - Z)$	=	Bond dissociation energy of bond Y - Z.
$\Delta H(1)$	=	Heat of reaction (1).
$\Delta H_f^\circ(X)$	=	Heat of formation of substance X.
k_1	=	Rate constant of reaction (1).
R_X	=	Rate of formation of product X.
$R_X\ (1)$	=	Rate of formation of product X by reaction (1).
R	=	Alkyl radical.
R	=	Gas constant.
ΔS_1	=	Entropy change of reaction (1).
T	=	Absolute temperature.
$[X]$	=	Concentration of X.

CONTENTS

CHAPTER I

INTRODUCTION

THE REACTIONS OF ALKYL RADICALS

Early work on the reactions of alkyl radicals in the gas phase was largely qualitative. Quantitative work was only made possible as refined analytical techniques were introduced. Low temperature distillation enabled some work on methyl and ethyl radicals to be carried out, and mass spectrometry enlarged the field to higher alkyl radicals. However the development of gas chromatography (1955) solved the analytical problems more completely. Most of the information on C_3 and C_4 radicals has been obtained in this way.

At the start of the present work in 1959, many relative rate constants for disproportionation, metathetical, addition and decomposition reactions of alkyl radicals were known. The information on methyl radicals was most complete, but all radicals up to C_4 had been studied to some extent. However there is a lack of reliable absolute rate constants for the higher alkyl radicals. The present work includes an attempt to determine an absolute rate constant for the isopropyl radical.

1.1 RADICAL SOURCES

Metal Alkyls. Radicals produced by the pyrolysis of metal alkyls have been studied to a considerable extent[1] on a qualitative basis. However the temperature required for pyrolysis is too high

to study many of the radical reactions of interest.

The photolysis of metal alkyls has been used for quantitative work. The photolyses of dimethyl and diethyl mercurys are more complicated than those of the corresponding ketones, but they are reasonable radical sources. They have generally been used to corroborate results from the ketone photolyses.

A further disadvantage is the probability that radicals from this source are "hot", that is not in thermal equilibrium with their surroundings. Caule and Steacie[3] found C_2 and C_4 products from the photolysis of di-n-propyl mercury at 100°C. With added inert gas, the C_3 and C_6 products yield increased at the expense of C_2 and C_4. At lower pressures of di-n-propyl mercury the effect was reversed.

Also the higher mercury alkyls are involatile and thermally unstable and the photolysis mechanism is complicated by heterogeneous thermal reactions.

Metal alkyls other than those of mercury have provided sources of alkyl radicals,[2] but have only yielded qualitative results.

The Photolysis of Ketones. The mechanisms of the photolyses of acetone[4,5] and diethyl ketone[6] are well-established. They are clean sources of methyl and ethyl radicals, acetone in particular has been widely used.

Unfortunately the photolysees of higher ketones are more complicated. At least two primary photolytic processes occur in the photolysis of ketones containing γ hydrogen atoms.

e.g. $CH_3CH_2CH_2COC_3H_7 \xrightarrow{h\nu} CO + 2nC_3H_7$ I

$\xrightarrow{h\nu} C_2H_4 + CH_3COC_3H_7$ II

$\xrightarrow{h\nu} CH_3 + C_2H_4COC_3H_7$ III

Type I is the desired split to give alkyl radicals. Type II is an intramolecular rearrangement, in which the bond between α and β carbon atoms is broken, and a γ hydrogen atom is transferred to the α carbon atom. The olefin produced is also a decomposition product of the alkyl radical, and so complicates the interpretation of results. This type of primary process has been observed in the photolyses of methyl n-butyl ketone,[7,8,99] methyl n-propyl ketone,[7,63] methyl n-amyl ketone,[7] di-n-propyl ketone,[9] di-isobutyl ketone[10] and di-s-butyl ketone.[10] However the photolyses of methyl isopropyl ketone,[7] di-isopropyl ketone[11] and di-t-butyl ketone[10] which contain no γ hydrogen atoms, yield the alkyl radicals cleanly.

The relative importance of process II is greater for ketones with larger numbers of γ hydrogen atoms.[10] Processes analagous to II have been observed in the photolyses of all ketones, aldehydes, esters and carboxylic acids containing hydrogen atoms in the γ position with respect to the carbonyl group, which have so far been investigated. It has never been observed where such hydrogen atoms were absent.

A primary photolytic act of type III has also been postulated by Kraus and Calvert,[10] but it is of minor importance.

In spite of these complications, the higher ketones have been used fairly extensively, especially in the study of low temperature reactions such as disproportionation and combination. They are a good source of isopropyl and t-butyl radicals.

Mercury Photosensitised Reactions

The mercury photosensitised decomposition of the paraffins has

been extensively investigated as a source of alkyl radicals.[12] Unfortunately the parent molecules are the same as the products of some of the more interesting reactions of the radicals. Their presence prevents the measurement of these products. Also in the case of propane or a butane, a mixture of radicals is produced, although secondary and tertiary radicals are produced in preference to primary.

Nevertheless most of the early quantitative work on alkyl radical decompositions was made by Bywater and Steacie,[13] using this source. When the disadvantages are taken into account their results[14] are confirmed by later work. The most successful study of the decomposition of ethyl was made using this source, in this case only one radical is produced.

The only quantitative work produced so far on cyclic alkyl radicals is the work of Gunning et al.[15,16,17] on the mercury photosensitised decomposition of cyclopentane, methyl cyclopentane and cyclohexane. The disproportionation reaction relative to combination has been studied.

The mercury photosensitised addition of hydrogen atoms to olefins has also been used extensively to produce alkyl radicals. However the source has the same disadvantages as the photosensitised decomposition of paraffins. The addition of a hydrogen atom to an olefin is a highly exothermic reaction, the radicals produced are "hot",[18] and the results produced for radicals generated in this way, often differ considerably from those for radicals in thermal equilibrium with their surroundings. Adding inert gas to the system[19] partly

solves the difficulty however.

Azo compounds. Azomethane has been photolysed and pyrolysed to produce methyl radicals. Azoethane similarly produces ethyl radicals, but these sources have no advantages over ketone photolyses. The selective photolysis of azomethane at 3660 Å in n-butyraldehyde has been used by Calvert and Sleppy,[20] to generate n-propyl radicals in thermal equilibrium with their surroundings. However the temperature range is restricted, and in many systems the presence of methyl radicals may be undesirable, so the method is of limited application.

The photolyses of the azopropanes have been recently investigated. Kiem and Kutschke[21] made a detailed study of the photolysis of azo-isopropane and concluded that the only photolytic decomposition gave nitrogen and alkyl radicals directly. The deactivation of azo-isopropane by internal conversion of energy was also important. Kerr and Calvert[22] photolysed azo-n-propane and found it a clean source of n-propyl radicals. However the reaction mechanism at high temperatures is somewhat complicated by addition of the radical to the nitrogen double bond.

Minor sources. The photolyses of esters and acids are complex, they yield alkoxyl or hydroxyl radicals as well as alkyl radicals. If the alkyl side-chain contains γ hydrogen atoms an olefin is also produced.[23] Thus they are unsuitable as alkyl radical sources.

Thynne[24,25] has recently selectively photolysed ketone and formate mixtures. The ketone is photolysed at a wavelength greater than 3000 Å, at which the formate is unaffected. The radical from

the ketone then initiates the chain decomposition of the formate. The alkyl radicals from the formate are generated in thermal equilibrium with their surroundings.

Di-t-butyl peroxide has been used as a thermal source of methyl radicals. It is useful for studying metathetical reactions, where the substrate would be photolysed, for instance it was used in work on the abstraction of the carbonyl hydrogen atom from aldehydes by methyl.[26]

Photolysis of Aldehydes. The primary processes in the photolyses of the lower aldehydes have been well established by Blacet et al.[27,28] They found four types of primary process:-

$$\text{e.g. } CH_3.CH_2.CH_2CHO \xrightarrow{h\nu} \begin{array}{ll} C_3H_7 + CHO & \text{I} \\ C_2H_4 + CH_3CHO & \text{II} \\ C_3H_8 + CO & \text{III} \\ CH_3 + C_2H_4CHO & \text{IV} \end{array}$$

Process I predominates at long wavelengths, at shorter wavelengths II and III become important, IV is a minor process. Process II only occurs in aldehydes containing γ hydrogen atoms. The existence of these primary acts is confirmed for ethyl, propyl and butyl radicals by Gruver and Calvert,[29] and Trotman-Dickenson et al.,[30-35] although the latter work was not quantitative for the photolytic act.

However a high proportion of alkyl radicals are produced by the chain decomposition of the aldehyde, because the carbonyl hydrogen atom has a high metathetical reactivity.

$$R + RCHO = RH + RCO$$

$$RCO = R + CO$$

As the temperature is raised these chains become longer, and the effect of the stable products from the photolysis is minimised. Also a large proportion of the radicals will be generated in thermal equilibrium with their surroundings. The source is better described as the photo-initiated chain decomposition of aldehydes.

This source has been widely used to study the combination, disproportionation, abstraction from aldehyde, addition to double bonds and decomposition reactions of ethyl,[33] n-propyl,[30] isopropyl,[31] n-butyl,[32] s-butyl[29] and t-butyl[34] radicals. The present work has extended its use to isobutyl.[35] The source is not suitable for the study of metathetical reactions unless the substrate is heavily deuterated.

1.2 COMBINATION REACTIONS

The Combination of Like Radicals

Although many alkyl radical combination reactions are known, few rate constants have been measured. It is easy to measure the rate of formation of the dimer, but difficult to measure the concentration of the radical. Where reliable rate constants for combination are lacking, arbitrary Arrhenius parameters have been selected to express the results. The values chosen were

$E = 0$ k. cal. mole.$^{-1}$ and $A = 10^{14.0}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$

Thus most rate constants for alkyl radical reactions are only known relative to this assumption. However when reliable absolute values are available, it will be simple to rescale the results.

Methods of determing absolute rate constants, and the values for

alkyl radicals known at the start of the present work are reviewed in the following. The determination of the absolute rate of combination of isopropyl, the validity of the system used, and the comparison of experimental alkyl radical combination rate constants with theory is considered later, in the discussion.

Methods of determining radical concentration and absolute rate constants. A physical method of determining radical concentration uses electron-spin resonance, possible because all radicals possess an unpaired electron. The method is specific for a particular species and can determine concentration at a particular point in the reaction system. Intensity of absorption depends upon the number of radicals present, so relative concentrations can easily be measured, but a reference measurement is needed for absolute determinations. However the method is not sufficiently sensitive to measure radical concentrations of about 10^{-13} or 10^{-12} moles. cm.$^{-3}$ normally encountered in gas phase reactions.

Another method of measuring radical concentration consists of introducing radicals produced by pyrolysis in a flow system directly into the ionisation chamber of a mass spectrometer. The flow system is connected to the mass spectrometer via a pin hole leak. The sensitivity of the radical must be calibrated previously by decomposing known amounts of a substance giving the required radical, in the mass spectrometer. The method is specific, but the experimental technique is difficult. Experimental conditions require a very low pressure of organic vapour in an inert gas, and may introduce pressure effects for lower alkyl radicals.

A technique developed by Moseley and Robb[36] involves recording the observed pressure change in the gas, resulting from the adiabatic temperature changes caused by reaction. The pressure changes are observed by a sensitive diaphragm type manometer, with sensitivity better than 10^{-4} mm. Hg and time lag in response less than 10^{-3} seconds.

It may be possible for radical concentrations in a combination reaction to be determined indirectly, by knowledge of the rate constant of another reaction of the radical. This method was used by Miller and Steacie[37] who considered the recombination of methyl and its reaction with nitric oxide. The accuracy is of course limited by the accuracy with which the rate of the competing reaction is known.

Some indications of the values of combination rate constants may be gleaned from the study of cross-combinations over a wide temperature range, particularly where the autocombination rate of one radical is well-established, as in the case of methyl. Such indications will be considered under cross-combinations.

The method of measuring radical concentrations most commonly used is that of Intermittent Illumination. This is produced by regularly chopping the beam of actinic light, using a rotating disc from which a sector has been removed. The method measures the mean lifetime of the radicals under steady conditions. Then, if their rate of production is known, their concentration can be calculated. A full review of the method has been given by Melville and Burnett.[38]

It is necessary for the mechanism of the photolysis to be well-

understood, otherwise results may be misleading. For the method to be applicable, the radical concentration in the system must depend upon a power of the light intensity under steady illumination, lower than the first. In practice this is fulfilled if two radicals are mutually destroyed by combination or disproportionation, then the radical concentration depends on the square root of the light intensity. However Shepp[39] has produced a modified intermittent illumination theory, considering terminations of both first and second order with respect to radical concentration. With this refinement the method may be applied to any system in which first order termination is measurable and does not exceed about 40% of the second order termination.

The theory of intermittent illumination provides data for the variation of the ratio of radical concentrations under intermittent and steady illumination, with the length of light flash in units of radical lifetimes. The variation of this ratio with the length of light flash in seconds is determined experimentally. The displacement between the theoretical and experimental relations is a measure of the mean radical lifetime in seconds. Some reaction, first order with respect to radical concentration, must be used to determine the relative concentration under intermittent and steady illumination. The system may include such a reaction, or it may be introduced by adding a marker. If the radical is removed by this reaction, conditions must be adjusted so that second-order termination predominates.

The rate of production of radicals may be determined directly

if the quantum efficiency of their production and the absorbed light intensity is known. However it is simpler to equate the rate of production with that of destruction, which can usually be easily measured. When radical concentrations have been determined it is a simple matter to find rate constants.

Corrections to allow for non-uniform light intensity have been considered by Burns and Dainton,[40] but are unimportant unless the substance photolysed is strongly absorbing. They also evaluated a correction to allow for a time of partial illumination, caused by the finite time taken for the sector edge to chop the light beam. If the sector speed is high, or the ratio of sector width to light beam width is high this correction is negligible. Melville and Burnett[38] give a correction to be applied if pyrolysis accompanies photolysis.

Absolute rate constants for alkyl radical combinations

Methyl radicals. The recombination of methyl has been most widely explored. The destruction of methyl radicals is by combination only, because disproportionation to give an olefin is impossible.

The most reliable value of k_c, the combination rate constant, was determined by Kistiakowsky and Roberts[41]

$$k_c = 10^{13.57} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at 165°C with a pressure of 30 mm. They photolysed acetone using intermittent illumination. A similar value was found for trideuteromethyl.

This was preceded by a similar determination by Gomer and Kistiakowsky[42] using acetone and dimethyl mercury, the agreement between the sources was very good. They found

$$k_c = 10^{13.65} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

with an activation energy of E = 0 ± 700 cal. mole.$^{-1}$ between 125 and 220°C, total pressure between 10 and 50 mm.

Shepp[39] has applied his correction for first order termination to the work of Kistiakowsky and Roberts and his corrected value for the rate constant is

$$k_c = 10^{13.34} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

between 125 and 175°C. This is the currently accepted value.

The rotating sector technique has also been applied to the photolysis of acetaldehyde.[43,44,45] The results for the rate of the chain-breaking step are in fair agreement with the acetone work. However the ethane was not measured, but the rate of radical production estimated using quantum efficiencies obtained from other work. The mechanism was doubtful under the conditions used, and the reaction was merely followed by a pressure change. The agreement with the accepted value is probably fortuitous.

Mosely and Robb[36] applied the technique of observing the pressure change due to the adiabatic temperature changes caused by reaction, to the mercury photosensitised decomposition of acetone. They found

$$k_c = 10^{13.60} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at room temperature and a total pressure of 75 mm. Considering experimental difficulties the agreement is reasonable.

Miller and Steacie[37] photolysed dimethyl mercury in a circulating system in the presence of nitric oxide. They found the radical concentration by measuring consumption of nitric oxide, and used the rate constant for the combination of methyl with nitric oxide,

from Forsyth's[46] work using a Paneth mirror technique. Later Durham and Steacie[47] repeated the latter determination using a refined technique. The corrected value obtained for methyl combination was

$$k_c = 10^{12.04} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at room temperature and a pressure of 4.5 mm. The effect of pressure on this value is discussed later.

The mass spectrometric method was used by Lossing, Ingold and Tickner,[48] using the pyrolysis of dimethyl mercury. They found

$$k_c = 10^{12.71} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

between 850 and 975°C, with a pressure of 15 mm. helium carrier gas and a few microns of dimethyl mercury. Refining the technique and extending the temperature range to between 161 and 814°C, Ingold and Lossing[49] found

$$k_c = 10^{13.11} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at a similar pressure.

The latter results do not agree with the acetone photolysis value. When pressure effects are considered the disagreement is less serious. Methyl radicals contain only one heavy atom, so their combination rate may depend markedly on pressure, due to third body effects. Analagous effects are well known in atomic combinations.

Marcus and Rice[51,52] believe that the fall-off in the methyl radical combination rate should become important at a pressure of a few millimetres. This is experimentally confirmed by Kistiakowsky and Roberts,[41] who found that the combination rate fell to one-third of its high pressure value, at 1 mm. Ingold, Henderson and Lossing[50] also observed a pressure dependence in the region 3.4 to 15 mm.

Gomer and Kistiakowsky[42] observed that the results of Steacie et al.[37,47] are compatible with the acetone photolysis data, when pressure effects are considered. If the pressure dependence of the reaction of methyl with nitric oxide is the same as for methyl combination, then the value of Durham and Steacie[47] would be increased by a factor of 200 at high pressures. A factor of 30 would be sufficient to reconcile the two results, so the methyl-nitric oxide combination is probably less pressure dependent than methyl combination, a reasonable assumption.

Similarly the low value of Ingold and Lossing[49] may be due to the low third-body efficiency of helium. Their negative temperate coefficient may be caused by the decrease in the lifetime of energy-rich ethane molecules with rising temperature, predicted by Rice-Kassel theory of unimolecular reactions. Their stabilization by collision may be a rate-determining step.

Thus the work on methyl combination is in substantial agreement.

The combination of the analagous trifluoromethyl radical has been studied by Ayscough[54] by the rotating sector method, using hexafluoroacetone as a radical source. Methane was added, and the abstraction of hydrogen by trifluoromethyl was used to estimate relative trifluoromethyl concentrations. A Shepp type correction for first order disappearance of trifluoromethyl was applied. The rate constant at 127°C and 40 mm. of hexafluoroacetone was

$$k_c = 10^{13.36} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

Ethyl radicals. Ivin and Steacie[55] photolysed diethyl mercury using the rotating sector. Their value at 80 mm. and 150°C was

$$k_c = 10^{13.20} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

This rate constant combined with a calculated collision frequency shows that the activation energy cannot exceed 0.65 k. cal. mole.$^{-1}$

However the rate constant was calculated assuming that the ratio of disproportionation to combination, k_d/k_c, for ethyl = 0.40. Other reliable determinations (see 1.3) give k_d/k_c a value of about 0.15. This raises the combination rate constant, giving

$$k_c = 10^{13.28} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

Bradley, Melville and Robb[77] have estimated the collision efficiency of the mutual destruction of ethyl radicals, using a system in which a molybdenum trioxide surface competed with the gas phase reaction to remove radicals. The radicals were produced by the addition of atomic hydrogen, from the mercury photosensitised dissociation of hydrogen molecules, to ethylene. At 20°C they found

$$k_c + k_d = 10^{13.42} \text{ mole.}^{-1}\text{cm.}^3 \text{ sec.}^{-1}$$

with a total pressure of 23 mm. However they used a value of $k_d/k_c = 0.46$ to calculate the amount of gas phase ethane from the butane production. This termination rate constant is in reasonable agreement with that of Ivin and Steacie.[55] However the high disproportionation ratios of radicals from both sources introduce doubt in the determination of k_c. In both cases the radicals were probably "hot".

A more complete study on the photolysis of diethyl ketone, using the rotating sector, was carried out by Shepp and Kutschke,[56] they found

$$k_c = 10^{14.20} \exp. (-2000 \pm 1000/RT) \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

at pressures between 10 and 50 mm., and temperature between 50 and 150°C. They assumed $k_d/k_c = 0.12$, and made a correction for first order termination.

n-Propyl radicals. Whiteway and Masson[57] determined the rate constant for n-propyl combination using the rotating sector photolysis of di-n-propyl ketone. At 100°C and a pressure of 12 mm., they found

$$k_c = 10^{15.78} \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

This value is higher than the calculated collision rate by a factor of about 25. The authors estimate it may be high by a factor of at least 20. No first order termination correction was made, but this would affect k_c by about a factor of 2 only. The system will contain a small number of methyl radicals, produced by the photolysis of methyl n-propyl ketone which will be obtained with ethylene from the primary photolysis. The authors suggested that the analysis for propane, carried out by low temperature distillation, may be inaccurate, because the propane from disproportionation was a comparable amount to the propane from abstraction, used to estimate relative radical concentration. Little reliance should be placed on this determination.

The Combination of Unlike Radicals. In a system containing two different alkyl radicals, A and B, three combination reactions may take place:-

$$2A = A_2 \ldots k_{aa}$$
$$2B = B_2 \ldots k_{bb}$$
$$A + B = AB \ldots k_{ab}$$

If none of these reactions has an activation energy, then the ratio $k_{ab}/(k_{aa}\, k_{bb})^{\frac{1}{2}}$ should equal 2, by the simple collision theory of

chemical kinetics. Results obtained are summarised in Table 1.2 to which a few explanatory notes are added. Where the ratio was determined over a substantial temperature range, this range is quoted.

Notes:-

a) Mean of several scattered runs between 29 and 169°C.

b) This figure was calculated from the results on the photolysis of methyl ethyl ketone below 170°C. The amount of ethane by methyl combination was calculated from the yield of methane and from the rate constant for attack of methyl radicals on the ketone. This constant had been found by photolysing azomethane with the ketone.

c) Based on a few non-concordant runs.

d) In this reaction system, where the addition of methyl radicals to ethylene was the primary consideration, the low value for the rate constant ratio is undoubtedly due to the formation of n-hexane, other than by n-propyl combination.

e) The results were very scattered but show no trend.

f) Calculated by Kerr and Trotman-Dickenson[75] from the yields of n-butane, isopentane and 2:3 dimethyl butane formed in the photolysis of isopropyl propionate.

g) Calculated by Kerr and Trotman-Dickenson,[75] nC_6F_{14} was estimated by the method of the original authors. The values are rather scattered.

Within experimental limits the only value which differs significantly from 2 is that between ethyl and perfluoropropyl, which is a very polar radical.

TABLE 1.2 COMBINATION OF UNLIKE RADICALS

Radicals A	Radicals B	$k_{ab}/(k_{aa}k_{bb})^{\frac{1}{2}}$	Temperature Range °C	Reference	Note
Methyl	CD_3	1.9	-	58	-
Methyl	CF_3	1.5	-	59	a
Methyl	Ethyl	1.9	25 - 240	60	b
		2.0	-	61	-
CD_3	Ethyl	1.8	27 - 200	62	-
Methyl	n Propyl	2.1	-	7	-
		2.6	-	63	c
		1.4	-	64	d
CD_3	$CH_3CH_2CD_2$	1.8	25 - 82	65	-
Methyl	Isopropyl	1.9	-	78	-
Methyl	n Pentyl	1.6	-	76	-
Methyl	Acetyl	1.7	-	58	-
		2.2	0 - 58	66	-
CD_3	CD_3CO	2.0	-	65	-
Methyl	Acetonyl	1.5	100 - 285	67	e
CF_2Cl	CF_2ClCF_3	2.2	-	68	-
CF_3	n C_3F_7	1.8	100 - 207	72	-
Ethyl	n Propyl	1.9	54 - 198	30	-
Ethyl	Isopropyl	2.0	50 - 200	31	-
		2	-	69	f
Ethyl	$CF_3CF_2CF_2$	3.2	-	70	g
Ethyl	Pentanonyl	1.7	100 - 250	71	-
n Propyl	n Butyl	2.2	100 - 207	32	-
Isopropyl	n Butyl	1.8	-	32	-
Ethyl	t Butyl	1.9	-	93	-
Isopropyl	t Butyl	2.0	-	93	-

The temperature coefficient of the ratio $k_{ab}/(k_{aa}\ k_{bb})^{\frac{1}{2}}$ is a measure of $E_{ab} - \frac{1}{2}(E_{aa} + E_{bb})$, the activation energy difference. In the ten cases shown where the temperature dependence of the ratio has been studied, it is independent of temperature. This sets limits on some of the activation energies of cross-combination. For instance in the cross-combination of methyl and ethyl,[60] E_{aa} is established as $E = 0 \pm 700$ cal. mole.$^{-1}$,[42] and E_{bb} as $E = 2000 \pm 1000$ cal. mole.$^{-1}$.[56] Hence E_{ab} cannot exceed 1800 cal. mole.$^{-1}$.

Pritchard and Dacey[73] claim that the rate constant ratio for methyl and trifluoromethyl is temperature dependent. They estimate that

$$E_{ab} - \tfrac{1}{2}(E_{aa} + E_{bb}) = -1070 \pm 100 \text{ cal. mole.}^{-1}$$

They believe that the trifluoromethyl combination may have a small activation energy due to the polarity of the radical, and show that the relative A factors can be predicted in terms of transition state theory.[74] However none of the well-established values in Table 1.2 can be similarly predicted. The work of Sieger and Calvert[59] on the photolysis of methyl trifluoromethyl ketone was not accurate, but it showed no definite trend between 29 and 169°C. Also Ayscough[54] showed that trifluoromethyl recombine on every collision at 127°C, therefore the reaction is unlikely to have an appreciable activation energy.

The cross-combination results in general indicate, but do not prove, that these combinations occur on every collision. The required collision diameters are probably slightly different from those required for the calculation of transport properties.

1.3 DISPROPORTIONATION

When two alkyl radicals react they may combine to form the dimer, or disproportionate to form a paraffin and an olefin.

$$2R = R_2 \quad \ldots k_c$$

$$\text{and} \quad 2R = (R + H) + (R - H) \quad \ldots k_d$$

Disproportionation involves the transfer of a hydrogen atom and is therefore a type of metathetical reaction. However disproportionations have very small activation energies, and A factors of the same order as combinations, so it is convenient to consider them separately. Disproportionations are highly exothermic compared with metatheses, hence the activation energies are small.

Disproportionation of Like Radicals. From the equations above we have

$$R_{R2} = k_c [R]^2$$

$$\text{and} \quad R_{(R-H)} = R_{(R+H)} = k_d [R]^2$$

where R_x is the rate of formation of X

$$\therefore \quad k_d/k_c = R_{(R+H)}/R_{R2} = R_{(R-H)}/R_{R2}$$

It is generally most convenient to measure the rate of formation of the olefin, because the paraffin may be produced by metathetical reactions of the radical. However when the radical source is the addition of hydrogen to the olefin, the rate of paraffin formation must be used. This is a disadvantage of this radical source.

The absolute rate constant for the disproportionation of ethyl radicals was determined by the photolysis of diethyl ketone with intermittent illumination[56]

$$k_d = 10^{13.56} \text{ exp. } (-2000 \pm 1000/RT) \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

Other disproportionation rate constants have been determined relative to assumed combination rate. Table 1.3A gives a summary of the results which have been obtained for the ratio k_d/k_c, to which a few explanatory notes are added.

Notes:-

a) Limiting value at high pressure of hydrogen, at lower pressures k_d/k_c is higher.

b) Single run.

c) Authors later placed doubt on this value, because of the difficulty in the mass spectrometric analysis of isobutene in the presence of large amounts of isobutane.[91]

d) It appears that insufficient allowance was made for the production of isobutene by chain decomposition of the ketone. The results are compatible with those of reference 35. See Chapter III.

e) The calculation of the relative amounts of 1-pentene from auto-disproportionation and cross-disproportionation with methyl, was based on the doubtful results of Kraus and Calvert,[10] which relate k_d/k_c for butyls to the number of abstractable hydrogen atoms. In any case this relation was only postulated for auto-disproportionations between alkyl radicals containing the same number of carbon atoms.

TABLE 1.3A AUTODISPROPORTIONATION

Radicals and Source	Temperature °C	k_d/k_c	Reference	Note
ETHYL				
Diethyl ketone P	100 - 250	0.12	79	-
	180 - 230	0.14	80	-
2:2:4:4-Tetradeutero diethyl ketone P	24 - 180	0.1	81, 97	-
Propionaldehyde P	50 - 315	0.15	33	-
Diethyl mercury P	75 - 200	0.42	55	-
T	350	0.13	82	-
C_2H_4 + H	20	0.1	83	-
	20	0.15	84	-
CH_2D_2 + H	20	0.15	85	-
C_2D_2 + H	20	0.14	86	a
n PROPYL				
Di-n-propyl ketone P	100 - 150	0.13	57	-
n-Butyraldehyde P	25 - 190	0.16	30	-
Methyl n propyl ketone P	25	0.15	65	-
Azo-n-propane P	25 - 130	0.16	22	-
Di-n-propyl mercury P	30 - 108	0.3	3	-
ISOPROPYL				
Di-isopropyl ketone P	25 - 150	0.63	11	-
Methyl isopropyl ketone P	100	0.67	78	-
Isobutyraldehyde P	20 - 260	0.65	31	-
Azo-isopropane P	30	0.53	88	-
	60 - 127	0.53	21	-
Di-isopropyl mercury T	230 - 440	1	89	-
Propylene + H	20	0.5	83	-

TABLE 1.3A (continued)

Radicals and Source	Temperature °C	k_d/k_c	Reference	Note
n-BUTYL				
n-Valeraldehyde P	100	0.7	32	-
n-Butyl formate MS	70 - 195	0.94	24	-
Di-n-butyl mercury P	220	1.5	90	b
sec BUTYL				
Di-s-butyl ketone P	100	2.3	10	-
1 Methyl butyraldehyde P	25	0.61	29	c
2-Butene + H	20	1.5	83	-
	25	0.6	92	-
ISOBUTYL				
Di-isobutyl ketone P	78 - 108	0.42	10	d
Isovaleraldehyde P	25 - 125	0.17	35	-
t-BUTYL				
Di-t-butyl ketone P	100	4.59	10	-
	100	3.2	93	-
Pivalaldehyde P	27 - 230	4.38	34	-
		3.2	93	-
Isobutene + H	20	2.2	83	-
n PENTYL				
Methyl n Pentyl ketone P	63	0.2	76	e
CYCLOPENTYL				
Cyclopentane - H	30	0.2	15	-
METHYL CYCLOPENTYL				
Methyl Cyclopentane - H	30	0.4	16	-

TABLE 1.3A (continued)

Radicals and Source	Temperature °C	k_d/k_c	Reference	Note
CYCLOHEXYL				
Cyclohexane - H	30	0.5	17	-

P = Photolysis. T = Thermal decomposition.
+ H = Mercury photosensitised addition of H to olefins.
- H = Mercury photosensitised decomposition of paraffins.
MS = Methyl radical sensitised chain decomposition.

The values obtained include some remarkable disagreements, where the same radical has been obtained from different sources. Alkyl mercury compounds seem to be unsatisfactory sources, they give high disproportionation ratios and are probably "hot" radicals. The mercury photosensitised addition of hydrogen to olefins suffers from the same disadvantage. For both these sources it has been shown[19,86] that k_d/k_c is higher at low pressures, where the energy content of the radical is higher. Also the latter source is apt to produce a mixture of radicals.

The other values are in good agreement for ethyl and propyl. The n-butyl radical will be discussed later. Although the ketone and aldehyde photolyses yield different values for isobutyl, the results are compatible, see note (d). The most reliable value for s-butyl is probably that from the ketone source. The t-butyl radical presents difficulty.

In general, disproportionation reactions have zero activation energy, which is intuitively expected for a radical-radical reaction. However a temperature coefficient has been reported for n-butyl,[32]

$$k_d = 10^{14.6} \text{ exp. } (-1300/RT) \text{ mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

This rate constant was determined by the photolysis of n-valeraldehyde. Similar radical sources provide results in excellent agreement with ketone sources for ethyl,[33] n-propyl[30] and isopropyl.[31] However Thynne[24] has repeated the determination, using the methyl sensitised chain decomposition of n-butyl formate, and found no temperature coefficient. This source definitely provides thermally equilibrated radicals, however it is not clear how he distinguished between olefin formed from autodisproportionation and cross-disproportionation with methyl.

Ausloos and Steacie[94] observed that if the combination rate constants for the two propyl radicals are assumed equal, the ratio of their disproportionation rate constants was approximately equal to the ratio of the number of hydrogen atoms available for disproportionation. They considered only hydrogen atoms whose abstraction gives the required olefin directly.

Kraus and Calvert[10] found a similar relation for butyl radicals, considering isobutyl, s-butyl and t-butyl. The value for n-butyl determined by Thynne[24] fits the pattern. However recent work[35,93] casts considerable doubt on the values for isobutyl and t-butyl, and it seems there is no such simple pattern.

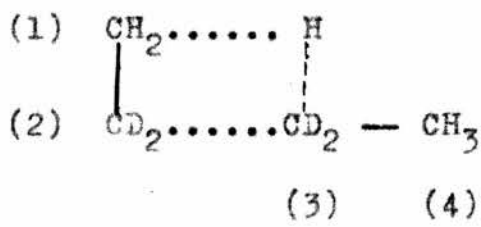
Various theories have been proposed to explain the mechanism of disproportionation. The hydrogen atom transferred in the ethyl

disproportionation has been identified by the photolysis of 2:2:4:4-tetradeutero diethyl ketone.[81,95] The olefin from the reactions of CH_3CD_2 radicals contained over 90% CH_2CD_2. This was interpreted as the result of a head-tail mechanism, with the following activated complex:

$$CH_3.CD_2...H....CH_2.CD_2$$

However this complex is very similar to that of the attack of methyl on ethane. The A factor for this abstraction is 10^{11} mole.$^{-1}$ cm.^{3} sec.$^{-1}$, and for the disproportionation is $10^{13.6}$, which is surprising if the activated complexes are similar. On the other hand disproportionation and combination A factors are similar, suggesting a head-head mechnaism.

A four-centre head-head mechanism which explains the results has been proposed by Bradley[96] and Kerr and Trotman-Dickenson.[75]



Bradley calculated that if the tetrahedral bond angle was distorted by 20° or more the hydrogen on carbon (1) would be nearer carbon (3) than those on carbon (2). The activation energy for the four-centre decomposition could be provided by the highly exothermic dimerization. This theory explains why radicals which have an excess of energy from their formation process have abnormally high disproportionation ratio.[19,86] The absence of disproportionation in the liquid phase,[87] where deactivation by collision is extremely rapid, is also explicable in terms of this theory.

Further evidence for this mechanism has been provided by Bradley.[96] He calculated the value of $S_c^* - S_d^*$, the difference between the apparent entropies of activation for combination and disproportionation, for a series of auto and cross-disproportionations from experimental values of k_c/k_d. From transition state theory the rate constant at a particular temperature depends only upon the entropy of activation, if the activation energy is zero, or if it is the same for the two reactions compared it will cancel when differences are calculated. He then showed that there was a linear relationship between $S_c^* - S_d^*$ and $S_d - S_c$, the entropy difference between the products of disproportionation and combination. Laidler and Wojciechowski[53] point out that this type of relation is expected on the basis of the above mechanism. After the activated complex is formed the subsequent reaction path will depend only on the relative entropies, $S_c^* - S_d^*$ of the configurations leading to the two types of product. The energies will be irrelevant because the activated state has already been surmounted.

Disproportionation of Unlike Radicals. When a mixture of two unlike radicals are present they may cross-disproportionate in two ways. It is convenient to define Δ as the ratio k_d/k_c. The symbol $\Delta(Et, Pr^i)$ refers to the reactions

$$C_2H_5 + C_3H_7 = C_2H_6 + C_3H_6$$

$$\text{and} \quad C_2H_5 + C_3H_7 = C_5H_{12}$$

whereas the symbol $\Delta(Pr^i, Et)$ refers to

$$C_2H_5 + C_3H_7 = C_2H_4 + C_3H_8$$

$$\text{and} \quad C_2H_5 + C_3H_7 = C_5H_{12}$$

A large number of cross-disproportionation ratios have been determined and the more reliable values are listed in Table 1.3B. Boddy and Robb[83] have carried out an extensive study of cross-disproportionation, using the mercury photosensitised addition of hydrogen to olefins as a radical source. The results are in poor agreement with values from ketone photolyses and methyl sensitised formate decompositions. Where both the latter sources have been used to determine one Δ, the results are consistent. Because of the inherent disadvantages of Boddy and Robb's source, their results have been omitted from the table.

Note:-

a) This determination suffers from the same uncertainty as that of note (e) in the autodisproportionation table.

To compare values of Δ for auto and cross-disproportionation, the autodisproportionation values should be divided by two. This is because when two like radicals disproportionate either may be the attacking radical, thus the rate constant is equivalent to the sum of two cross-disproportionation rate constants.

An attempt has been made to fit the established data into a simple pattern. Kerr and Trotman-Dickenson[75] divided each value of by $[H]$, the number of abstractable hydrogen atoms which give an olefin directly. They then plotted log $\Delta(Alk, Alk')/[H]$ against log $\Delta(Alk, Alk)/[H]$ where Alk and Alk' are two unlike alkyl radicals. It was found that the values of $\Delta(Me, Alk')/[H]$ where Alk' was ethyl, isopropyl and t-butyl, gave a straight-line, slope 0.5. However data

recently available[24,25,93] do not fit such a simple relation. It seems unlikely that the values of Δ will conform to any simple pattern. Perhaps if the absolute values of the relevant combination and cross-combination rate constants were known, the position would be clearer.

All cross-disproportionations investigated over a temperature range show no temperature coefficient.

TABLE 1.3B CROSS-DISPROPORTIONATION

Radicals and Source	Δ (Alk, Alk')	Reference
METHYL, Δ (Me, Alk)		
Alk:-		
Ethyl		
Methyl ethyl ketone P	0.04	94
Acetone + 2:2:4:4 Tetradeutero diethyl ketone P	0.06	61
Ethyl formate MS	0.06	98
n-Propyl		
n-Propyl formate MS	0.10	98
Isopropyl		
Acetone + Methyl isopropyl ketone P	0.22	91
Isopropyl formate ES	0.20	98
n-Butyl		
n-Butyl formate MS	0.15	24
t-Butyl		
Acetone + Pinacolone P	0.70	91
n-Pentyl		
Methyl n-pentyl ketone P	0.10[a]	76
ETHYL, Δ (Et, Alk)		
Alk:-		
n-Propyl		
n-Propyl formate ES	0.16	98
Isopropyl		
Isopropyl formate ES	0.43	25
t-Butyl		
Diethyl ketone + Di-t-butyl ketone P	0.49	93

TABLE 1.3B (continued)

Radicals and Source	Δ (Alk, Alk')	Reference
ISOPROPYL, $\Delta(Pr^i, Alk)$		
Alk:-		
Ethyl		
Isopropyl formate ES	0.15	25
t-Butyl		
Di-isopropyl ketone + Di-t-butyl ketone P	0.70	93
t-BUTYL, $\Delta(Bu^t, Alk)$		
Alk:-		
Ethyl		
Diethyl ketone + Di-t-butyl ketone P	0.31	93
Isopropyl		
Di-isopropyl ketone + Di-t-butyl ketone P	0.67	93

P = Photolysis.

MS = Methyl sensitised decomposition, methyl from photolysis of acetone >3000 Å.

ES = Ethyl sensitised decomposition, ethyl from photolysis of diethyl ketone >3000 Å.

1.4 METATHESIS

The only type of metathesis which has been studied extensively for alkyl radicals is that which involves the transfer of a hydrogen atom:

$$R + HX = RH + X$$

Other types of metathesis which have been studied include abstraction from methyl nitrite by methyl:

$$CH_3 + CH_3NO_2 = CH_3NO + CH_3O$$

which was observed by Jest and Phillips,[161] and the transfer of a halogen atom when an alkyl radical abstracts from an alkyl or benzyl halide. The latter reactions have been summarised by Szwarc.[160]. The present discussion will be confined to transfer of a hydrogen atom.

This is undoubtedly the most widely studied class of alkyl radical reaction. However most of the work has concerned methyl and ethyl radicals, comparatively little study of abstraction by higher alkyl radicals has been made. Large numbers of methyl radical abstractions from a wide range of organic substrates have been studied. The methods employed and the results obtained have been summarised by Trotman-Dickenson.[100,101] In the present discussion methyl radical results will be omitted, except for the purpose of comparison with ethyl.

Metatheses may be divided into two classes a) abstraction from the radical source, b) abstraction from an added organic substrate. The latter class has been studied only for methyl and ethyl radicals.

The general mechanism for abstraction from the radical source

is as follows:-

$$\text{Source} = R$$

$$2R = R_2 \qquad (1)$$

$$2R = RH + (R - H) \qquad (2)$$

$$R + \text{Source} = RH + \text{other radical} \qquad (3)$$

A photolytic source of radicals is most commonly employed. R_2 is the radical dimer, RH a paraffin and (R - H) an olefin. We wish to measure the rate of reaction (3). The total rate of formation of the paraffin is equal to R_{RH} (2) plus R_{RH} (3), where R_{RH} (2) is the rate of formation of the paraffin from reaction (2). However if disproportionation is the only source of the olefin, then R_{RH} (2) is equal to $R_{(R-H)}$ (2). Hence R_{RH} (3) is obtained by subtraction. If the source is an aldehyde the scheme is complicated by the formation of the paraffin in the photolytic act. However this becomes less important as the temperature is raised.

From reaction (1) $[R] = R_{R_2}{}^{\frac{1}{2}}/k_1{}^{\frac{1}{2}}$

and from (3) $k_3 = R_{RH}(3)/[R][\text{Source}]$

Hence $k_3/k_1{}^{\frac{1}{2}} = R_{RH}(3)/[\text{Source}]\, R_{R_2}{}^{\frac{1}{2}}$

The concentration of the radical source may be regarded as constant for small percentages of conversion, otherwise a mean value is taken. Thus k_3, the abstraction rate constant, is determined relative to k_1, that for combination. If this is not known reasonable values for the parameters for combination are assumed.

In the case of ethyl radicals, where hydrogen abstraction from added substrates has been measured, the radicals have been generated

by the photolysis of diethyl ketone, or the corresponding fully deuterated ketone. The mechanism is well-established.[80]

$$C_2H_5COC_2H_5 + h\nu = 2C_2H_5 + CO$$

$$2C_2H_5 = C_4H_{10} \quad (4)$$

$$2C_2H_5 = C_2H_6 + C_2H_4 \quad (5)$$

$$C_2H_5 + (C_2H_5)_2CO = C_2H_6 + C_2H_5COC_2H_4 \quad (6)$$

$$C_2H_5 + C_2H_5COC_2H_4 = C_4H_9COC_2H_5 \quad (7)$$

Reaction (7) occurs only below 250°C and at high light intensity. The material balance derived from this scheme has been checked experimentally and confirms the mechanism. From the above scheme,

$$k_6/k_4^{\frac{1}{2}} = \frac{R_{C_2H_6} - R_{C_2H_4}}{[\text{ketone}]\, R_{C_4}^{\frac{1}{2}}}$$

$$= \left(\frac{R_{C_2}}{R_{C_4}} - \frac{2k_5}{k_4}\right) \frac{R_{C_4}^{\frac{1}{2}}}{[\text{ketone}]}$$

The value of k_5/k_4 for ethyl was found to be 0.14,[80] and that for perdeuteroethyl was 0.10,[97] these values were independent of temperature and ketone pressure. Hence the rate constant k_6, derived in the above manner, is known with reasonable certainty. The values for ethyl[79,80,106] and perdeutero ethyl[97,108] have been checked by several determinations.

If a substrate molecule XH, containing abstractable hydrogen atoms, is added to the diethyl ketone, the additional reaction (8) may occur

$$C_2H_5 + XH = C_2H_6 + X \quad (8)$$

If the radical X does not lead to C_2 or C_4 products, then we have

$$k_8/k_4^{\frac{1}{2}} = \left(\frac{R_{C_2}}{R_{C_4}} - \frac{2k_5}{k_4}\right)\frac{R_{C_4}^{\frac{1}{2}}}{[XH]} - \frac{[(C_2H_5)_2CO]}{[XH]}\,\frac{k_6}{k_4^{\frac{1}{2}}}$$

If the deuterated ketone is used we obtain a simpler expression. Abstraction from the parent ketone yields C_2D_6, and abstraction from XH is the only source of C_2D_5H.

$$\text{Hence}\quad k_8/k_6 = \frac{R_{C_2D_5H}\ [(C_2D_5)_2CO]}{(R_{C_2D_6} - R_{C_2D_4})\ [XH]}$$

$$\text{and}\quad k_8/k_4^{\frac{1}{2}} = \frac{R_{C_2D_5H}}{R_{C_4}^{\frac{1}{2}}[XH]}$$

In practice the ketone used by Boddy and Steacie[97,102] contained isotopic impurities and corrections to the simple expression were necessary, these however were small. The deuterated ketone permits the study of abstraction from substrates such as butanes, which would otherwise be impossible. The results obtained from these studies are included in Table 1.4A.

General Features of Metatheses of Alkyl Radicals

In general it has been found that methyl radicals abstract tertiary hydrogen atoms faster than secondary, and secondary faster than primary. This order has also been observed for ethyl by Boddy and Steacie[97] considering abstraction from iso-butane, n-butane and neopentane. This is expected because of the relative strengths of the bonds broken. It is interesting to compare results obtained for the abstraction of the same hydrogen by methyl and ethyl. These are

summarised in the following table. To set the results on a comparative basis, a correction for primary abstraction has been made using the neopentane data, then the rate has been divided by the number of abstractable hydrogen atoms of the type of C-H bond in question.

TABLE 1.4B

	C_2D_5 [97,102]			CH_3 [114,115]		
Substrate	E	$10^{-6}k_{182^o}$	$10^{-6}k_{182^o}$/active H	E	$10^{-6}k_{182^o}$	$10^{-6}k_{182^o}$/active H
Primary C-H						
Neopentane	12.6	0.31	0.026	10.0	3.3	0.28
Secondary C-H						
n Butane	10.4	2.3	0.52	8.3	11	2.3
n Hexane	10.1	4.4	0.53	8.1	17	2.5
Cyclo-hexane	10.4	5.6	0.47	8.3	22	1.8
Tertiary C-H						
Isobutane	8.9	4.5	4.3	7.6	22	20

E is in k. cal. mole.$^{-1}$, k in mole.$^{-1}$ cm.^{3} sec.$^{-1}$

The Rate factors are based on $k_c = 10^{13.3}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for CH_3, $k_c = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for C_2D_5

In general the activation energies for abstraction by ethyl are about 2 k. cal. mole.$^{-1}$ higher than those for methyl. If we consider the reactions

$$CH_3 + RH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_4 + R \qquad (1) \qquad \Delta H_1$$

$$C_2D_5 + RH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2D_5H + R \qquad (2) \qquad \Delta H_2$$

then assuming $D(C_2H_5 - H) = D(C_2D_5 - H)$ we may calculate that $\Delta H_2 - \Delta H_1 = 5$ k. cal. mole.$^{-1}$

Now $\Delta H_2 - \Delta H_1 = E_2 - E_{-2} - E_1 + E_{-1}$

$= 2 - (E_{-2} - E_{-1})$

$\therefore E_{-1} - E_{-2} = 3$ k. cal. mole.$^{-1}$

The activation energies of a pair of the reverse reactions have only been determined in two cases. Where R is trideuteromethyl the activation energy for attack on methane is 14.0 k. cal. mole.$^{-1}$,[116] and for attack on ethane is about 11.3 k. cal. mole.$^{-1}$.[117,118] Therefore in this case the results present a consistent picture. In contrast the perfluoropropyl radical abstracts from methane and ethane with the same activation energy. However the high polarity of this radical makes it unsuitable for comparative purposes.

A striking feature of Table 1.4B is the rate of abstraction from secondary C-H bonds. For both methyl and ethyl this is constant for both alkanes, and varies little even for a cyclane. Jackson and McNesby[135] have noted a similar result in the abstraction of primary hydrogen atoms from alkanes by trideuteromethyl. Work by McNesby et al.[117,136-7] and Tijnen[118] has provided information on the rates

of abstraction by CD_3 to form CD_3H, from C_2H_6, CH_3CD_3, $CH_3CD_2CH_3$ and $CH_3CD_2CD_2CH_3$. Rates were measured relative to abstraction from the radical source, hexadeutero acetone. The rate of primary hydrogen abstraction depended solely on the number of abstractable hydrogens, not on the alkane. No similar measurements have yet been made for ethyl.

James and Steacie[80] found an increase in the rate of abstraction by ethyl, in the series n-heptane, 1-heptene, 1-heptyne, which shows how the rate of abstraction of a constituent hydrogen atom may be affected by the structure of the substrate. However they found that the activation energies for abstraction from a series of alkenes were the same within experimental error. Therefore it seems likely that the small variations in rates in this series are due to differences in the A factors. This is in contrast to abstraction from alkanes by ethyl, where rate differences are explained by different activation energies. This contrast is also found in abstraction by methyl from alkenes and alkanes. No explanation of these findings has yet been proposed.

Table 1.4C shows that the activation energies for abstraction by n-propyl and isopropyl are generally similar. This is surprising considering the strengths of the bonds broken when the two radicals are formed from propane, differ by three k. cal. $mole.^{-1}$ or more. However definite comparisons cannot yet be made because the substrates are different.

Table 1.4D shows a few results obtained for abstraction by butyl radicals from their parent aldehydes. Although there are some

variations in the Arrhenius parameters for the abstraction of the carbonyl hydrogen, the rate constants at 182°C are remarkably constant. This is surprising because the bond formed when methyl abstracts hydrogen is stronger than that formed when t-butyl abstracts. Birrell and Trotman-Dickenson[26] have shown that methyl abstracts the carbonyl hydrogen of a series of aldehydes at the same rate, therefore this effect is not explained by the effect of the alkyl side-chain on the ease of losing the carbonyl hydrogen. A similar effect has been observed for the abstraction of hydrogen by alkyl radicals from their parent azo compounds.[22] The abstraction of the carbonyl hydrogen of the aldehyde is a highly exothermic reaction (D (CH_3CO - H) = 84 k. cal. mole.$^{-1}$), the high exothermicity of all these abstractions may account for the constancy of the rates.

With few exceptions the experimental A factors for abstraction by all alkyl radicals are close to 10^{11} mole.$^{-1}$ cm.^{3} sec.$^{-1}$. Estimates made from transition state theory for methyl, trideutero and trifluoro methyl radical abstractions from hydrogen and n-alkanes, agree well with experimental values.[119,120] However accurate estimates of A factors for higher alkyl radicals cannot be made from transition state theory. The barrier to free rotation in the activated complex is not known, and where a large group is concerned the entropy associated with this rotation is considerable and may cause an appreciable error in the calculation of the A factor.

TABLE 1.4A METATHESES OF ETHYL RADICALS

Reactant	Source	E k.cal.mole^{-1}	log A mole^{-1}cm.^{3}sec.$^{-1}$	10^{-6} k at 182°	Ref.
Hydrogen	$(C_2D_5)_2CO$ P	11.3	11.9	3	102
Deuterium	Diethyl ketone P	13.3	12.3	1	103
n Butane	$(C_2D_5)_2CO$ P	10.4	11.4	2	97
Isobutane	$(C_2D_5)_2CO$ P	8.9	11.0	5	97
Neopentane	$(C_2D_5)_2CO$ P	12.6	11.6	0.3	97
n Hexane	$(C_2D_5)_2CO$ P	10.1	11.5	4	102
Cyclohexane	$(C_2D_5)_2CO$ P	10.4	11.8	6	102
Cyclohexene	Diethyl ketone P	8.2	11.8	72	80
n-Heptane	Diethyl ketone P	10.6	12.0	8	80
1-Heptene	Diethyl ketone P	8.3	11.5	32	80,104
1-Heptyne	Diethyl ketone P	7.6	11.2	36	80
1-Octene	Diethyl ketone P	8.3	11.5	32	80
Trans-4-octene	Diethyl ketone P	8.7	11.8	42	80
Cyclohexa-1,3 diene	Diethyl ketone P	5.4	10.8	160	104
Propionaldehyde	Propionaldehyde P	5.9	11.1	182	33
	D.T.B.P. and Propionaldehyde T	7.6	11.8	141	105
Methyl ethyl ketone	Methyl ethyl ketone P	8.0	11.3	28	94
Diethyl ketone	Diethyl ketone P	7.8	11.4	45	79,80, 106
	Azoethane P	7.6	11.3	44	107
$(CH_3CD_2)_2CO$	$(CH_3CD_2)_2CO$ P				
$(CH_3C\underline{D}_2)_2CO$		8.7	11.9	51	81
$(C\underline{H}_3CD_2)_2CO$		11.7	11.7	4	81
$(C_2D_5)_2CO$	$(C_2D_5)_2CO$ P	9.0	11.3	8	97,108
Azoethane	Azoethane P	7.5	11.2	40	109
		8.0	11.6	50	110
Diethyl mercury	Diethyl mercury P	6.2	10.6	42	55

The Rate factors are based on $k_c = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for ethyl combination. The atoms underlined are attacked in metathesis.

D.T.B.P. is Di-t-butyl peroxide.

T = radicals produced by thermal decomposition.

P = Photolysis.

TABLE 1.4C METATHESES OF PROPYL RADICALS

Reactant	Source	E k.cal. mole.$^{-1}$	log A mole.$^{-1}$ cm.^{3} sec.$^{-1}$	10^{-6} k 182°	Reference
n-PROPYL RADICALS					
n-Butyraldehyde	n-Butyraldehyde P				
n $C_3H_7C\underline{H}O$		6.7	11.3	120	30
n $C_3\underline{H}_7CHO$		10.8	11.3	1	30
Di-n-propyl ketone	Di-n-propyl ketone P	6.5	10.7	38	9
Azo-n-propane	Azo-n-propane P	7.9	11.6	60	22
ISOPROPYL RADICALS					
Hydrogen	Propylene + H	12.5			111
Isobutyraldehyde	Isobutyraldehyde P				
iso $C_3H_7C\underline{H}O$		6.3	11.3	186	31
iso $C_3\underline{H}_7CHO$		9.5	11.2	4	31
Di-isopropyl ketone	Di-isopropyl ketone P				
$((CH_3)_2C\underline{D})_2CO$		9.3	11.1	4	11
$((C\underline{H}_3)_2CD)_2CO$		11.7	11.8	5	11
Azoisopropane	Azoisopropane P	6.5	10.4	19	21, 88
PERFLUORO n-PROPYL RADICALS					
Hydrogen	$(C_3F_7)_2CO$ P	12.3	12.6	5	112
Deuterium	$(C_3F_7)_2CO$ P	13.8	12.8	2	112
Methane	$(C_3F_7)_2CO$ P	9.5	11.0	3	70
Ethane	$(C_3F_7)_2CO$ P	9.2	12.2	60	70
Cyclohexene	$(C_3F_7)_2CO$ P	5.2	8.1		113

Rate factors are based on $k_c = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for propyl combination.

+ H, radicals produced by mercury photosensitised addition of hydrogen to olefin.

TABLE 1.4D METATHESES OF BUTYL RADICALS

Reactant	Source	E k.cal. mole.$^{-1}$	log A mole.$^{-1}$ cm.^{3} sec.$^{-1}$	10^{-6} k 182°	Reference
n BUTYL RADICALS					
n Valeraldehyde	n Valeraldehyde P	5.4	10.9	200	32
sec BUTYL RADICALS					
1-methyl butyraldehyde	1-methyl butyraldehyde P	4.9	10.7	220	29
ISOBUTYL RADICALS					
Isovaleraldehyde	Isovaleraldehyde P				
$C_4H_9C\underline{H}O$		6.5	11.7	380	35
$C_4\underline{H}_9CHO$		12.7	12.6	3	35
Di-isobutyl ketone	Di-isobutyl ketone P	7.6	11.4	55	10
t-BUTYL RADICALS					
Pivalaldehyde	Pivalaldehyde P				
$C_4H_9C\underline{H}O$		4.3	10.5	270	34
$C_4\underline{H}_9CHO$		10.0	11.9	50	34

Rate factors based on $k_c = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for butyl combination.

1.5 ADDITION TO MULTIPLE BONDS

The addition of alkyl radicals to multiple bonds has long been recognized, but comparatively few quantitative determinations of these reactions have been made. In addition to the usual difficulty of measuring radical concentration, there is the problem of measuring the rate of formation of the product, itself a radical. The simplest case is addition to ethylene:

$$R + CH_2 = CH_2 = R.CH_2.CH_2.$$

The product alkyl radical may then abstract from the radical source, react with R, or add to ethylene. It may also dimerize or disproportionate with itself, but these reactions are of minor importance. If the rate of the primary addition is to be accurately determined, all the further reactions of the radical product must be followed. Even in the case of a methyl radical addition the analysis is somewhat complex.

In the gas phase there have been two general methods of approach; a) that involving a material balance of the attacking radical, and b) that involving the analysis of the reaction products of the resulting radical. The results obtained are summarised in Table 1.5A.

The addition of alkyl radicals to double bonds are the reverse reactions of alkyl radical decompositions. In the following section, 1.6, it will be shown how the activation energies of the two reactions may be compared to thermal data, and how the A factors may be related to entropy changes of the reaction.

Methyl Radical Additions. Mandelcorn and Steacie[121] studied the addition of methyl to a series of unsaturates, using a material balance method. The source of methyl was the photolysis of acetone, for which the mechanism is well-understood. Between 100 and 280°C the mechanism is

$$CH_3COCH_3 + h\nu = 2CH_3 + CO \quad (1)$$

$$2CH_3 = C_2H_6 \quad (2)$$

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \quad (3)$$

$$CH_3 + CH_2COCH_3 = C_2H_5COCH_3 \quad (4)$$

The material balance gives $\left(2R_{C_2H_6} + R_{CH_4} + R_{C_2H_5COCH_3}\right)/R_{CO} = 2.0$, where R_X is the rate of formation of X. This ratio has been found experimentally to be 1.90,[126] verifying the mechanism. When an unsaturate is present there will be an extra reaction

$$CH_3 + U = CH_3U \quad (5)$$

where U is the unsaturate. The presence of the unsaturate does not affect CO formation, therefore the material balance becomes

$$\left(2R^*_{C_2H_6} + R^*_{CH_4} + R^*_{C_2H_3COCH_3} + R'_A\right)/R^*_{CO} = 1.9$$

where R'_A is the rate of formation of the CH_3U radical, and * indicates the presence of unsaturate. Hence R'_A can be found by subtraction. However this expression neglects the consumption of methyl radicals by the reaction

$$CH_3 + CH_3U = CH_3UCH_3 \quad (6)$$

This will be more important at low temperatures, and R'_A will be greater than R_A the true rate of addition, so the above expression will give a low value for the activation energy, E'_A.

Before the development of gas chromatography it was difficult to determine methyl ethyl ketone in a large excess of acetone, therefore a second approach was made. The production of ethane and methane is much more important than that of methyl ethyl ketone. Therefore the authors equated $(2R^{*}_{C_2H_6} + R^{*}_{CH_4} + R''_A)/R^{*}_{CO}$ with $(2R_{C_2H_6} + R_{CH_4})/R_{CO}$. The difference between R''_A and R'_A depends on $R_{C_2H_5COCH_3}/R_{CO}$, and the extent to which this ratio is decreased by the addition reaction. R''_A is less than R'_A and the difference is greatest at high temperatures when addition is faster. Hence $E''_A < E'_A < E_A$.

A third approach was also used, Mandelcorn and Steacie[121] assumed that only one molecule of unsaturate is converted to higher-boiling material for each methyl which adds to the unsaturate. This ignores consumption of unsaturate by addition of the product radical or acetonyl. The resulting rate, R'''_A, is therefore higher than the true rate. The discrepancy will be greatest at high temperatures, therefore $E'''_A > E_A$.

The agreement between results for R''_A and R'''_A for addition to ethylene, propylene, butadiene and acetylene is fairly good.

The addition of methyl to ethylene has also been studied by Brinton[64] who analysed the reaction products of the propyl radical. The source of methyl was the thermal decomposition of di-t-butyl peroxide. He attempted to limit the polymerisation of ethylene to the initial addition, by keeping the ethylene concentration low.

Significant amounts of n-hexane were formed, which were attributed to the combination of n-propyl. However the ratio $R_{C_4H_{10}}/(R^{\frac{1}{2}}_{C_2H_6}\ R^{\frac{1}{2}}_{C_6H_{14}})$ for cross-combination was equal to 1.4. This ratio is generally close to 2.0 (see Table 1.2), and indicates that hexane was also formed by the addition of propyl to ethylene, followed by the combination of pentyl with methyl. Therefore the rate of propyl formation has probably been overestimated, particularly at high temperatures, and so the activation energy is probably slightly high. Brinton's value for the activation energy is higher than Mandelcorn and Steacie's, but the rate constants at 142°C are in good agreement.

The rate of methyl addition to ethylene has also been determined by polymerisation experiments. Raal and Danby[127] photolysed acetaldehyde in the presence of ethylene. Products were not analysed, but the overall pressure change and the rate of consumption of acetaldehyde were measured. Their activation energy, when calculated using the currently accepted value for methyl attack on acetaldehyde was 4.6 k. cal. mole.$^{-1}$. However the determination was based on a complicated steady state treatment, and the rates of the individual polymerisation steps could not be determined, so the method is not reliable. Landers and Volman[128] used the thermal decomposition of di-t-butyl peroxide as a source and also followed the reaction by overall pressure change. Their value for the addition activation energy was 8.2 k. cal. mole.$^{-1}$, in better agreement with the other values. However both these determinations depend on the interpretation of the polymerisation kinetics, and on

the activation energies of other reactions, so they are of doubtful significance.

The addition of methyl to acetylene has been determined by Mandelcorn and Steacie[126] by material balance, and by García Domínguez and Trotman-Dickenson[123] by analysis of the reaction products of the propenyl radical produced. The latter determination is to be preferred because it is more direct. The same value was also determined by Landers and Volman[128] who found an activation energy of 5.1 k. cal. mole.$^{-1}$ in good agreement with García Domínguez and Trotman-Dickenson, however this is probably fortuitous because of the limitations of their method.

Ethyl radical additions. A material balance method similar to that of Mandelcorn and Steacie[121] has been developed by James and Steacie[125] for the addition of ethyl to unsaturates. The radicals were generated by the photolysis of diethyl ketone, the mechanism below 250°C is given in section 1.4. From this the material balance obtained is

$$(R_{C_2H_6} + R_{C_4H_{10}})/R_{CO} = 1.0$$

which has been confirmed experimentally. When unsaturate is present an ethyl radical may add to the multiple bond producing a new radical. This will either react with a second ethyl radical, or form some stable product which involves the destruction of an ethyl radical. Thus two ethyl radicals are removed by each addition to the multiple bond. The material balance becomes $(R^*_{C_2H_6} + R^*_{C_4H_{10}} + R_A)/R^*_{CO} = 1.0$ where * denotes the presence of unsaturate, and R_A is the rate of addition to the multiple bond.

The results obtained by James and Steacie,[125] and by Brown and James[104] using the same method, are shown in Table 1.5A. Four classes of unsaturated hydrocarbons were studied, mono-substituted alkynes, mono-substituted alkenes, di-substituted alkenes and dienes. The activation energies fell into a distinct range for each class, although the difference between the last two classes was small.

The addition of ethyl to ethylene has been studied by three independent methods, each involving analysis of the products. Pinder and Le Roy[124] used the mercury photosensitised addition of hydrogen atoms to ethylene, as their source of ethyl. They measured the rate of addition by assuming all the butyl radicals formed combine with ethyl to give n-hexane, which introduces some uncertainty into the rate constant. Lampe and Field[122] used the photolysis of azoethane. They also assumed all butyl radicals combined with ethyl, in this case the assumption is very doubtful, because abstraction by butyl from the azoethane is neglected. This would affect the relative rate constant in two ways, not only would the rate of addition be underestimated, but butane from ethyl combination would be over-estimated. Since this effect will be more important at high temperatures their activation energy is probably low. Kerr and Trotman-Dickenson[33] generated ethyl by the photolysis of propion-aldehyde, and obtained a higher addition activation energy. Again there were complications due to butane being formed in two ways, however reasonable estimates for the proportion formed by butyl abstraction and ethyl combination were made. This is probably the most reliable value.

James and Steacie[125] found that the activation energy for addition of ethyl to a double bond decreased with increasing substitution of the double bond. For monosubstituted ethylenes the activation energy for addition is about 7 k. cal. mole.$^{-1}$, so that for ethylene itself is probably higher than seven.

The addition of ethyl to acetylene has been determined by García Domínguez and Trotman-Dickenson[123] analysing the products. The energy of activation was lower than that for addition of ethyl to 1-heptyne, in contrast to the decrease with increasing substitution found in the alkene series.

Higher Alkyl Radical Additions. The addition of higher alkyl radicals to ethylene and acetylene has been studied by Trotman-Dickenson et al.[30-4,123] The radicals were generated by the photolysis of the corresponding aldehydes. Analysis was simplified by adjusting conditions so that the great majority of product radicals abstracted from the aldehyde. Small corrections were made for further addition to ethylene, dimerisation and disproportionation.

The most striking feature of the data is the constancy of the rate constants. The values for A factors and activation energies show more variation, but this may be partly due to experimental error. In the acetylene series the activation energy decreases with increasing complexity of the attacking radical.

An interesting feature of the acetylene work was an isomerisation of the radical produced when isopropyl and t-butyl add to ethylene.[123] In the former case the products included some 1-pentene as well as the expected 3-methyl 1-butene. This was attributed to

the following isomerisation before abstraction to form the olefin.

$$iC_3H_7 + CH \equiv CH = \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \!\!\!\

The results for methyl addition to mono, di, tri and tetra substituted ethylenes in solution may be compared to the gas phase work by James and Steacie,[125] on the addition of ethyl to similar unsaturates. The results are summarised in Table 1.5B, after Trotman-Dickenson.[133] Rates are normalised to 1.0 for the monosubstituted ethylenes. In both cases the 1:2 disubstituted ethylene was less reactive than the monosubstituted ethylene. However 1:1 disubstituted compounds were more reactive, so the decrease in reactivity in the former case must be due to steric hinderance. Tri and tetra substituted compounds are even less reactive for the same reason. In general trans disubstituted ethylenes are more reactive than the corresponding cis compound.

The work in solution has only yielded rate constants for addition, k_a^1, relative to rate constants for abstraction from the solvent, k_b^1. To place the gas phase results on a relative basis we may consider the rate of alkyl radical addition to ethylene, k_a, relative to abstraction from the parent aldehyde, k_b. The rate of abstraction is not influenced by the nature of the aldehyde since methyl abstracts from a series of aldehydes at identical rates.[26] The rates of addition of methyl,[64] ethyl,[33] isopropyl[31] and n-propyl[30] to ethylene in the gas phase are compared to the abstraction rates at 142°C, k_a/k_b. The work of Smid and Szwarc[134] in isooctane solution has measured the rate of addition of the same radicals to benzene, relative to abstraction from isooctane at 65°C, k_a^1/k_b^1.

Radical	Methyl	Ethyl	n-Propyl	Isopropyl
142°C k_a/k_b	0.45	0.33	0.50	0.63
65°C k_a^1/k_b^1	0.29	2.9	2.0	6.0 (35°C)

The lack of correlation between these two series of results is marked, it cannot be explained merely by the change from the gas phase to solution. The variations of the relative rates in solution may be partly explained by variations in k_b^1, the rate constant for abstraction from isooctane.

TABLE 1.5A ADDITION OF ALKYL RADICALS TO MULTIPLE BONDS

Reactant	Radical Source	E k. cal. mole.$^{-1}$	log A mole.$^{-1}$ cm.^{3} sec.$^{-1}$	10^{-6} k 142°C	Reference
METHYL RADICALS					
Ethylene	Acetone P	7.0	11.2	33	121
	D.T.B.P. T	8.7	12.1	33	64
Propylene	Acetone P	6.0	10.8	44	121
Butadiene	Acetone P	2.5	9.7	240	121
Acetylene	Acetone P	5.5	11.0	125	121
	Acetaldehyde P	7.8	11.4	20	123
ETHYL RADICALS					
Ethylene	Ethylene + H	5.5	10.0	13	124
	Azoethane P	5.5	10.3	26	122
	Propionaldehyde P	8.6	12.1	38	33
1-Hexene	Diethyl ketone P	6.8	10.9	21	125
1-Heptene	Diethyl ketone P	7.0	11.1	26	125,104
2:3:3-Trimethyl 1-butene	Diethyl ketone P	5.6	10.2	18	125
1-Octene	Diethyl ketone P	6.7	10.9	23	125
2:4:4-Trimethyl 1-pentene	Diethyl ketone P	5.7	10.6	40	125
2:3-Dimethyl buta-1,3-diene	Diethyl ketone P	4.5	11.5	-	104
Cyclohexa-1,3-diene	Diethyl ketone P	5.2	11.4	-	104
1-Heptyne	Diethyl ketone P	8.8	11.9	18	125
Acetylene	Propionaldehyde P	7.2	11.1	20	123
n PROPYL RADICALS					
Ethylene	n Butyraldehyde P	6.5	10.9	30	30

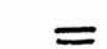
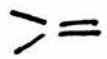
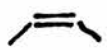
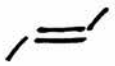
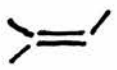
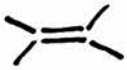
TABLE 1.5A (continued)

Reactant	Radical Source	E k. cal. mole.$^{-1}$	log A mole.$^{-1}$ cm.^{3} sec.$^{-1}$	10^{-6} k 142°C	Reference
ISOPROPYL RADICALS					
Ethylene	Isobutyraldehyde P	6.9	11.4	59	31
Acetylene	Isobutyraldehyde P	6.9	11.2	37	123
n BUTYL RADICALS					
Ethylene	n Valeraldehyde P	7.3	11.1	18	33
t BUTYL RADICALS					
Ethylene	Pivalaldehyde P	7.1	11.2	40	34
Acetylene	Pivalaldehyde P	5.4	10.7	71	123

Rate factors based on $k_c = 10^{13.3}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for methyl combination.

$k_c = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$ for other radical combinations.

TABLE 1.5B RELATIVE REACTIVITIES OF SUBSTITUTED DOUBLE BONDS

Group	Methyl 65°C, Solution		Ethyl 65°C, Gas Phase
	Ethylene 1.2	Ethylene 0.05	-
	Propylene 1.0	Styrene 1.0	1-Heptene 1.0
	Isobutene 1.6	1:1-Diphenyl ethylene 2.0	Methyl neopentyl ethylene 2.3
	cis-2-Butene 0.12	cis Stilbene 0.04	Cyclohexene 0.2
	trans-2-Butene 0.24	trans Stilbene 0.13	trans-di-Propyl ethylene 0.2
	-	Triphenyl ethylene 0.06	-
	-	Tetraphenyl ethylene 0.01	-
References	130	131, 132	125

1.6 DECOMPOSITION

Three types of alkyl radical decompositions have been studied quantitatively:

$$R = r + H \qquad (a)$$

$$R = r' + CH_3 \qquad (b)$$

$$R = r'' + C_2H_5 \qquad (c)$$

In each case r is an olefin molecule. These reactions apply to alkyls smaller than pentyl. The work of Sefton and Le Roy,[138] and Gordon and McNesby,[139] on the polymerisation of ethylene, induced by ethyl and methyl radicals respectively, provides qualitative evidence that n-pentyl, n-hexyl and n-heptyl radicals decompose to give an olefin and a smaller alkyl, in the latter cases a propyl radical.

It has generally been assumed that the mechanism involves the elimination of atomic hydrogen or an alkyl radical. However recently Gordon and Smith[140] have provided evidence for the molecular elimination of hydrogen. They photolysed hexadeuteroacetone in the presence of a series of alkanes. The high temperature reactions include:

$$CD_3 + RH = CD_3H + R \qquad (1)$$

$$CD_3 + CD_3COCD_3 = CD_4 + CD_2COCD_3 \qquad (2)$$

$$R = r + H \qquad (3)$$

$$H + RH = H_2 + R \qquad (4)$$

$$H + CD_3COCD_3 = HD + CD_2COCD_3 \qquad (5)$$

If the decomposition proceeds as is shown in (3) the only source of light hydrogen will be (4), providing there is no direct elimination of hydrogen from the alkane. Thus the ratios CD_3H/CD_4 and H_2/HD

would be expected to be similar at a particular temperature, because (1) to (5) are the only important sources of these methanes and hydrogen molecules. The latter ratio was in fact several times larger than the former, indicating that hydrogen was also formed by molecular elimination. This effect was observed for n-propyl, n-butyl and s-butyl radicals, but not for ethyl. No quantitative determination of the activation energy of molecular elimination was made, but it was thought to be about 30 k. cal. mole.$^{-1}$. These findings also show that some decomposition is via atomic elimination of hydrogen. The data given do not allow any assessment of the relative importance of the two types of decomposition.

The activation energies for decomposition are comparatively high; about 40-45 k. cal. mole.$^{-1}$ for reaction (a) and about 20-35 k. cal. mole.$^{-1}$ for reactions (b) and (c). The difference corresponds to the difference between the strengths of the C-H and C-C bonds.

Alkyl radical decompositions are not easy to measure. Thermally equilibrated radicals only start to decompose measurably above 200^{o}C, and at these temperatures there are a number of complicating side-reactions.

Various methods of generating the radicals have been used and will be discussed under the appropriate radical. However only two general methods have been widely used. Early work on alkyl radical decompositions was confined to the mercury photosensitised decomposition of paraffins, employed by Bywater and Steacie.[13] They produced radicals from ethane, propane, n-butane and isobutane at

temperatures between 30 and 500°C. However this method suffers from two inherent disadvantages. The effective reaction volume is not definitely known, estimates may be made of the percentage of mercury resonance radiation absorbed, but diffusion of radicals must also be considered. Also in all cases except ethane a mixture of radicals may be produced.

The photoinitiated chain decomposition of aldehydes has also been widely used to study radical decompositions by Gruver and Calvert[29] and Trotman-Dickenson et al.[30-35] This method is more direct because both products of the radical decomposition may be measured. Rates are measured relative to assumed combination rates in the usual manner, however at the high temperatures employed, the rate of dimer formation must be calculated from the rate of abstraction from the aldehyde, and known rate constants. Often small corrections for olefin formed in the primary photolytic act are necessary, and to measure reaction (a) corrections must be made for olefin formed by abstraction from the alkyl side-chain and subsequent decomposition of the radical formed.

The decompositions may be further divided into two types; those which yield the required olefin directly, and those which involve a rearrangement. The former type will be considered first. Table 1.6 summarises the results and relates kinetic and thermal data.

Decompositions Yielding the Olefin Directly.

Ethyl radicals are known to undergo decomposition by type (a) only:

$$C_2H_5 = C_2H_4 + H \quad (6)$$

The activation energies of the forward and reverse reactions are related to the heat of reaction as follows:

$$\Delta H\ (6) = E_6 - E_{-6}$$

Also $\Delta H\ (6) = \Delta H_f^o(H) + \Delta H_f^o(C_2H_4) - \Delta H_f^o(C_2H_5)$

but $\Delta H_f^o(C_2H_5) = \Delta H_f^o(C_2H_6) + D(C_2H_5 - H) - \Delta H_f^o(H)$.

$\therefore \quad \Delta H\ (6) = 2\Delta H_f^o(H) + \Delta H_f^o(C_2H_4) - \Delta H_f^o(C_2H_6) - D(C_2H_5 - H)$

The value of $\Delta H\ (6)$, and of the other heats of reaction of decompositions derived similarly, are shown in Table 1.6. The values of D(C - H) used in the calculations are also shown in the table. Hence for ethyl decomposition,

$$\Delta H\ (6) = 39 \text{ k. cal. mole.}^{-1}$$

from thermal data and

$$E_6 - E_{-6} = 39.5 - 6 \simeq 34 \text{ k. cal. mole.}^{-1}$$

from kinetic data, using the value of E_6 obtained by Bywater and Steacie[13] and E_{-6} equal to 6 k. cal. mole.$^{-1}$. This value is a reasonable estimate (see note (a) of Table 1.6). It seems that the decomposition activation energy has been underestimated.

Kerr and Trotman-Dickenson[33] found a value of 31 k. cal. mole.$^{-1}$ for E_6, using the photolysis of propionaldehyde to generate ethyl. This value is certainly too low. It is probably caused, at least in part, by an overestimation of n-butane formed, which was calculated from ethane formation and the known rate constants for abstraction from the aldehyde. At high temperatures ethyl will abstract from the alkyl side-chain, as well as from the carbonyl hydrogen, a process which has not been investigated for propionaldehyde. Ethane

formation in this way will be more important at high temperatures, leading to a low value of E_6. The rate constants at 400°C obtained by Bywater and Steacie,[13] and Kerr and Trotman-Dickenson,[33] are in good agreement, at this temperature the above complication will not be too serious.

n-Propyl radicals decompose in two ways:

$$n\ C_3H_7 = C_3H_6 + H \quad (7)$$

$$n\ C_3H_7 = C_2H_4 + CH_3 \quad (8)$$

The decomposition to propylene has been studied by Bywater and Steacie,[13] Kerr and Trotman-Dickenson[30] and Jackson and McNesby.[135] The three values for the activation energy are in reasonable agreement, although lower than thermal data predict. Little reliance may be placed upon the second determination, because the temperature range was restricted by the inconveniently rapid decomposition of n-butyraldehyde. On comparing the two types of n-propyl decomposition, Jackson and McNesby[135] found k_7/k_8 less than the value obtained by Kerr and Trotman-Dickenson[30] at a corresponding temperature. They criticized the aldehyde work on the grounds that some propylene may come from the increasing decomposition of the C_3H_6CHO radical, produced by abstraction from the alkyl side-chain, as the temperature is raised. Kerr and Trotman-Dickenson assumed the activation energy for this decomposition to be very low. If this criticism were valid, then at lower temperatures abstraction from the alkyl group would produce propane without propylene. Thus Kerr and Trotman-Dickenson would have overestimated the activation energy for abstraction of carbonyl hydrogen, and hence would have overestimated E_7 and E_8,

which is clearly not the case. In any case the discrepancy between the two studies lies largely in the decomposition to ethylene, not in that to propylene.

A large number of independent determinations of the decomposition to ethylene and methyl have been made. Early work yielded values close to 20 k. cal. mole.$^{-1}$ for E_8 and appeared to be consistent, nevertheless comparison with thermal data shows that this value is seriously low. Durham, Martin and Sutton[141] studied n-propyl formed by the sodium flame technique of Polanyi. Only a preliminary value for E_8 was published, so the results cannot be assessed. This is also true of the work of Masson,[9] using the photolysis of di-n-propyl ketone, because rate constants cannot be obtained from the data given. The value of Bywater and Steacie[13] may be low for the reasons mentioned earlier.

Kerr and Trotman-Dickenson[30] found a value of 25 k. cal. mole.$^{-1}$ for E_8, 6 k. cal. mole.$^{-1}$ lower than the thermal data predict, but this disagreement is less serious than that of the early work. The low value may be partly accounted for by the accumulation of small errors in estimates of abstraction rates from the aldehyde, and ethylene produced by the primary photolytic act.

Recent redeterminations of this activation energy favour a value between 30 and 35 k. cal. mole.$^{-1}$, in good agreement with thermal data. Calvert and Sleppy[20] generated n-propyl by the selective photolysis of azomethane in n-butyraldehyde. Thus ethylene from the primary photolytic act was avoided, but the rate could not be checked by methane formation. The activation energy

obtained was 34.9 k. cal. mole.$^{-1}$, this depended on the assumption that the activation energy for methyl combination with propyl was zero, as well as that for methyl combination.

Kerr and Calvert[22] generated n-propyl by the photolysis, and concurrent pyrolysis, of azo-n-propane. The primary photolytic act is free from ethylene production. Their value for E_8 was 34.5 k. cal. mole.$^{-1}$ in good agreement with Calvert and Sleppy, however the rate constants were lower. It was shown that this was probably due to the much lower pressure used in Kerr and Calvert's work. It is interesting to note that in the small temperature range in which the work of Kerr and Calvert,[22] and Kerr and Trotman-Dickenson,[30] overlap the rate constants are in excellent agreement.

A third recent study of this decomposition is that of Jackson and McNesby.[135] They generated n-propyl by the photolysis of hexa-deutero-acetone in the presence of 2:2 dideuteropropane. The rate of decomposition to ethylene was measured relative to that to propylene, and the results were rather scattered. An estimate of 31 k. cal. mole.$^{-1}$ was made for the activation energy. These three recent determinations are fairly consistent among themselves and compare well with thermal data, encouraging the belief that they are reliable.

Isopropyl radicals decompose directly thus:

$$i\ C_3H_7 = C_3H_6 + H \quad (9)$$

decomposition to ethylene involves rearrangement. Reaction (9) has been studied by Bywater and Steacie,[13] Kerr and Trotman-Dickenson[31] and Heller and Gordon,[11] the latter using the photolysis of di-iso-

propyl ketone. The latter two determinations are in good agreement, however once more the activation energy appears low when compared with thermal data.

n-Butyl radicals may eliminate a hydrogen atom or an ethyl radical directly:

$$n\ C_4H_9 = 1\text{-}C_4H_{10} + H \quad (10)$$

$$n\ C_4H_9 = C_2H_4 + C_2H_5 \quad (11)$$

There is no reliable information about reaction (10), the work of Bywater and Steacie[13] on the mercury photosensitised decomposition of n-butane would yield s-butyl radicals preferentially. The same limitation applies to their study of reaction (11), it is probably fortuitous that their results agree well with those of Kerr and Trotman-Dickenson[32] for this decomposition.

s-Butyl radicals may decompose directly thus:

$$s\ C_4H_9 = C_3H_6 + CH_3 \quad (12)$$

no study of the elimination of a hydrogen atom has been made. Apart from the work of Bywater and Steacie,[13] the only information comes from the photolysis of 1-methyl butyraldehyde by Gruver and Calvert.[29] They first put forward a rate constant of

$$k_{12} = 10^{11.7} \text{ exp. } (-24{,}000/RT) \text{ sec.}^{-1}$$

relative to the usual assumed butyl combination rate. However Calvert[142] later revised this value to

$$k_{12} = 10^{15.6} \text{ exp. } (-30{,}600/RT) \text{ sec.}^{-1}$$

The original value was calculated from methane formation, because the propylene analysis was less accurate. Allowance was

made for methane from the primary act. However studies of the iodine inhibited photolysis by Gruver and Calvert[143] detected no methane or methyl iodide. It was concluded that the methane in the uninhibited photolysis arose from the decomposition of a vibrationally excited 1-methyl butyraldehyde molecule, which would be deactivated by iodine. They believed this methane forming process was temperature dependent. Results were then recalculated making corrections for this methane source, and were also calculated on the basis of propylene formation. The corrected activation energy is in good agreement with thermal data, although the A factor seems improbably high. This type of correction is not applicable to the aldehyde photolyses of Trotman-Dickenson et al.,[30-5] because in each case the decomposition rate was measured by olefin formation, and checked by hydrogen, methane or ethane formation rates. Agreement was generally good.

Isobutyl radicals decompose directly in two ways:

$$i\ C_4H_9 = i\ C_4H_8 + H \quad (13)$$

$$i\ C_4H_9 = C_3H_6 + CH_3 \quad (14)$$

Work by Bywater and Steacie[13] on the photosensitised decomposition of isobutane is inconclusive because a mixture of isobutyl and t-butyl radicals will be formed. The study of these reactions by the photolysis of isovaleraldehyde[35] is described in Chapter III of this thesis. The values for the activation energies are low compared with thermal data.

t-Butyl radicals lose hydrogen directly:

$$t\ C_4H_9 = i\ C_4H_8 + H \quad (15)$$

loss of methyl involves rearrangement. Apart from the Bywater and Steacie[13] work, the reaction has been studied by the photolysis of pivalaldehyde by Birrell and Trotman-Dickenson.[34] The correlation between the experimental activation energy and thermal data shows a smaller discrepancy than usual. If the low activation energies found in the aldehyde work are partly due to an extra source of alkane at high temperatures, such as that from abstraction from the alkyl side-chain, this is expected. The rate of this abstraction has been unambiguously measured in the pivalaldehyde case, because this is the only case where all the hydrogen atoms of the side-chain are equivalent, thus no "extra" source of alkane can exist at high temperatures, when attack on different types of C-H bonds will be less discriminative.

The A factor for this decomposition seems improbably high.

Decompositions Involving Rearrangement.

Three decomposition reactions of type (b), involving rearrangement, have been studied:

$$i\ C_3H_7 = C_2H_4 + CH_3 \quad (16)$$

$$n\ C_4H_9 = C_3H_6 + CH_3 \quad (17)$$

$$t\ C_4H_9 = C_3H_6 + CH_3 \quad (18)$$

These three decompositions have been studied by the method of Bywater and Steacie,[13] where the radical species is in doubt, and also by Trotman-Dickenson *et al.*[31,32,34] using the aldehyde photolyses. The isopropyl decomposition has also been studied by Heller and Gordon,[11] using the photolysis of di-isopropyl ketone. Results are summarised in Table 1.6. The experimental activation energies

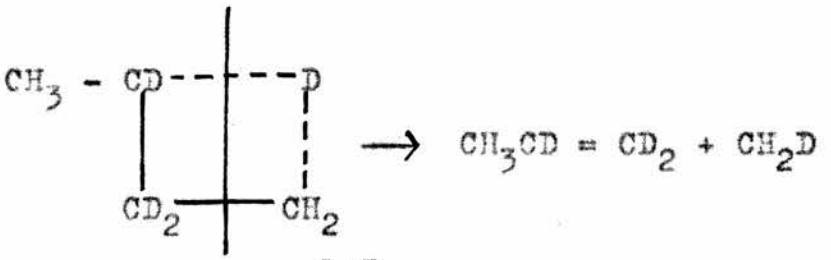
are always greater than the heats of reaction. However it is reasonable to suppose that some energy is involved in the rearrangement, so these activation energies have probably also been underestimated.

There is some doubt about the mechanism of these decompositions. If rearrangement occurs before decomposition we may expect to find products of the rearranged radical. This has not yet been done, but possibly the radical contains so much excess energy from the exothermic rearrangement that, at the low concentrations used, it decomposes before it is deactivated and before it can react in other ways. If this mechanism is valid the activation energies measured correspond to isomerization.

If rearrangement occurs during decomposition, then the addition of radicals to olefins should yield rearranged products. Brinton[64] and García Domínguez and Trotman-Dickenson[144] did not find a significant amount of isobutane from the addition of methyl, at high concentration, to ethylene. On the other hand the addition of alkyls to acetylene does yield rearranged products. Rearrangement occurs either during or following decomposition.

The decomposition of n-butyl to methyl and propylene is open to doubt. Early work by Frey and Hepp[145] on the pyrolysis of di-n-butyl mercury did not detect this reaction. However the photolysis of n-valeraldehyde[32] yielded a comparatively large rate constant for reaction (17). The work of McNesby, Drew and Gordon[146] on the photolysis of acetone in the presence of 2:2,3:3 tetradeutero-butane was interpreted as evidence against the isomerization of n-butyl.

The n-butyl radical generated is $CH_2CD_2CD_2CH_3$ and the propylene produced was all $C_3H_3D_3$. However Kerr and Trotman-Dickenson[75] pointed out that this result is consistent with a 4-centre rearrangement:



Later McNesby and Gordon[147] stated that no CH_2D_2 was found in their products, and so this mechanism is excluded. They suggested that the equivalent amounts of methane and propylene found in the photolysis of n-valeraldehyde, result from hydrogen abstraction from the side-chain followed by decomposition of the radical formed.

$$R + CH_3CH_2CH_2CH_2CHO = RH + CH_3\dot{C}H\ CH_2\ |\ CH_2CHO$$

$$R + CH_3CH_2CH_2CH_2CHO = RH + CH_3\ |\ CH_2\dot{C}H\ CH_2CHO$$

This possibility cannot be excluded but does not seem probable, because α hydrogen atoms will be most easily abstracted from the side-chain. Also there is no particular reason why the second case should yield propylene and not 1-butene. Abstraction from the alkyl side-chain was not measured in the case of n-valeraldehyde, in contrast to the majority of aldehyde studies. A further possibility is that n-butyl will abstract from the weakest bond in n-butane, at the temperatures at which decomposition was measured, forming a s-butyl radical which will decompose faster than n-butyl.

There is evidence from the work of Sefton and Le Roy,[138] and Gordon and McNesby[139] that larger n-alkyl radicals, C_5 to C_7, do

rearrange before or during decomposition.

The decompositions of isopropyl and t-butyl to methyl and an olefin are considerably slower than other decompositions, including that of n-butyl to methyl and propylene, which is expected if a rearrangement takes place. The validity of this isopropyl decomposition, studied by the aldehyde photolysis, is supported by the study of the photolysis of the corresponding ketone.[11] The generation of n-propyl by the reaction

$$i\ C_3H_7 + C_3H_8 = C_3H_8 + n\ C_3H_7$$

was excluded, because the yield of ethylene and methane was unchanged when propane was added to the photolysis mixture. The possibility of hydrogen atom addition to propylene followed by a rapid decomposition was rejected because this addition is principally to the end carbon atom of propylene, giving isopropyl.

Radical Decompositions and A factors

The A factor for a radical decomposition, A_d, is related to that of the reverse addition of a smaller radical to an olefin, A_a, and the entropy change of the reaction, ΔS, as follows:

$$\Delta S = R \ln A_d/A_a$$

The entropies of the radicals, and hence overall entropy changes, can be calculated with sufficient accuracy by standard methods. The A factors for the addition of methyl and ethyl to double bonds in the gas phase are of the order of 10^{11} mole.$^{-1}$ cm.^{3} sec.$^{-1}$, as is predicted by transition state theory. These values lead to a prediction of A factors of the order of 10^{13} sec.$^{-1}$ for the decom-

position of radicals, the normal value for unimolecular decompositions. The A factors for the loss of hydrogen approximate reasonably to this value on the whole. For the loss of methyl or ethyl, a wide variation in A factors is observed. In many cases this may be due to inaccuracies in determining the activation energies.

Radical Decompositions and Unimolecular Theory

Alkyl radical decompositions are unimolecular reactions, so they should provide an experimental test for unimolecular reaction theories. One of the main features of unimolecular reaction theory is that the unimolecular rate constant should be dependent upon the overall pressure of the system. Some preliminary work has been carried out on the pressure effect on the n-propyl decomposition. Kerr and Trotman-Dickenson[30] found that the rate constant for decomposition to methyl and ethylene was increased on increasing the aldehyde pressure or adding CO_2, and decreased at lower aldehyde pressures than normally used. The decomposition to propylene and hydrogen was less affected. Kerr and Calvert[22] found that the same rate constant increased as the pressure of azo-n-propane was increased. However on repeating part of Calvert and Sleppy's[20] work with azomethane and n-butyraldehyde, the rate constant increased slightly on halving the pressure. This latter effect is not understood, but is possibly due to non-homogeneous light absorption at the high pressures used.

TABLE 1.6 DECOMPOSITION OF ALKYL RADICALS

Radical and Reaction	C-H bond	ΔH	E_D (exp.)	log A_D (exp.)	k_D 400°C	Ref.	log A_{-D} (calc.)	log A_{-D} (exp.)	E_{-D} (exp.)	Ref.
LOSS OF H ATOM										
Ethyl	98	39	39.5	14.0+	16	13	13	13.5 (a)	4.1(a)	148
			31	11.2	13	33				
n Propyl	99	35	38 *	14.6*	200	13	13	14.4*(a)	5.0(a)	148
			35	13.6	159	30				
			37	14.1	120	135				
Isopropyl	94	40	38 *	14.6*	200	13	13	14.4*(a)	5.0(a)	148
			37	13.8	63	31				
			35	13.1	50	11				
n Butyl	101	31-3	high*	-	-	13	-	-	-	
s Butyl	94	38-40	high*	-	-	13	-	-	-	
Isobutyl	100	32	40 *	15.6*+	400	13	14	-	-	
			31	13.0	1000	35				
t Butyl	90	42	40 *	15.6*+	400	13	14	-	-	
			44	16.3	160	34				

E_A and A_D refer to the decomposition; E_{-D} and A_{-D} refer to the reverse reaction. * indicates results where it is uncertain which radical decomposes or is formed. + indicates maximum value of log A_D as calculated by Trotman-Dickenson[152] but corrected for $k_c = 10^{14}$ mole.$^{-1}$cm.^{3}sec.$^{-1}$ for radical combination. log A_{-D} (calc.) have been calculated from entropy changes.[153] Units; C-H bond, ΔH and E, k. cal. mole.$^{-1}$; A_D, k_D sec.$^{-1}$; A_{-D}, mole.$^{-1}$ cm.^{3} sec.$^{-1}$.

Note:

(a) These results are based on the Arrhenius parameters for the reaction of $H + H_2S = H_2 + HS$ derived by Darwent and Roberts,[149] which in turn depend on values of the parameters for the reaction $D + H_2 = DH + H$ obtained by Farkas and Farkas.[150] These latter results have been shown to be incorrect.[151] The activation energy for hydrogen addition to olefins is probably nearer 6-7 k. cal. mole.$^{-1}$.

TABLE 1.6 (continued)

Radical and Reaction	C-H bond	ΔH	E_D (exp.)	log A_D (exp.)	$10^{-2}k_D$ 400°C	Ref.	log A_{-D} (calc.)	log A_{-D} (exp.)	E_{-D} (exp.)	Ref.
LOSS OF METHYL										
n Propyl	99	23	20 *	9.2*+	5	13	6	12.1	8.7	64
			19	-	-	9,141				
			25.2	11.7	32	30				
			34.9	15.8	316	20				
			35.4	15.4	75	22				
			31	13.9	63	135				
Isopropyl	94	28	20 *	9.2*+	5	13	6	-	-	
			29.5	10.6	0.11	31				
			32.5	12.0	0.25	11				
n Butyl	101	18	23 *	11.2*+	55	13	8	11.2*	6.0*	121
			27.1	12.1	20	32				
s Butyl	94	25	23 *	11.2*+	55	13	8	11.2*	6.0*	121
			30.6	15.7	6030	142				
Isobutyl	100	21	18.5*	8.7*+	5	13	5	11.2*	6.0*	121
			26	12.8	200	35				
t Butyl	90	32	18.5*	8.7*+	5	13	5	-	-	
			46	16.0	0.10	34				
LOSS OF ETHYL										
n Butyl	101	19	23 *	11.2*+	55	13	8	12.1*	8.6*	33
			22.0	11.2	120	32				

CHAPTER II

GENERAL EXPERIMENTAL

The following description of the kinetic and analytical apparatus and chromatography system applies to the photolysis of isovaleraldehyde, the ketone photolyses and the photolysis of isobutyraldehyde/ethylene mixtures, used in the isopropyl combination work. Modifications to the apparatus and technique, employed for the latter work are discussed separately.

2.1 KINETIC AND ANALYTICAL APPARATUS

The apparatus as shown in Fig. 2.1 constituted a static system. The cylindrical quartz reaction vessel (R.V.) volume 155 $cm.^3$, length 10 cm., was connected to a conventional vacuum line. Pyrex glass was used throughout the apparatus. The pumping system consisted of a two stage mercury diffusion pump backed by a rotary oil pump, and was capable of reducing the pressure in the apparatus to about 10^{-5} mm. Hg. after about thirty minutes pumping. A 2 litre bulb was incorporated between the pumps as a backing volume.

The reaction vessel was also connected to the analytical section, which consisted of a train of three traps, T_1 - acetone dry ice, T_2 - liquid oxygen, and T_3 - liquid oxygen boiling at reduced pressure, and a three stage mercury diffusion pump (P) situated between T_1 and T_2. Non-condensable gases passing through these traps were pumped into a gas burette through a non-return mercury float valve (F) by means of a Toepler pump. The Toepler pump-gas

burette was also fitted with a McLeod gauge (M). The gas burette was calibrated by weighing mercury filling the various volumes. The sections of the burette as shown in Fig. 2.1 had the following volumes:

A	=	0.140 cm.^{3}
A + B	=	0.291 cm.^{3}
A + B + C	=	3.91 cm.^{3}
A + B + C + D	=	23.41 cm.^{3}
A + B + C + D + E	=	153.9 cm.^{3}

The three-way stopcock (S_1) at the top of the gas burette led on one side to the high vacuum line, and on the other to two U tubes and a small tube filled with iodine pentoxide. The first of the U tubes (U_1) contained activated silica gel, 30-120 mesh. The volume of this part of the apparatus was kept as small as possible by using capillary tubing where appropriate. Gases condensed in the low temperature distillation train were not passed into the gas burette, but were distilled several times through a short absorbent tube (A.T.) packed with 25-50 mesh powdered firebrick on which was suspended 25% by weight of a paste of sodium bisulphite in ethylene glycol.[154] This removed aldehyde before chromatographic analysis. These gases were then distilled into a tapped container, and subsequently into the injection system.

The apparatus also contained a storage bulb (S) with a trap and blow-off manometer. This was used to store ethylene, oxygen or nitric oxide. (R) was a reservoir for aldehydes or ketones. All reactants were stored over liquid oxygen or liquid nitrogen. A

mercury manometer (M_1) was attached on one side to the reaction vessel, and on the other to the high vacuum line. A low vacuum line was attached at the points marked L on Fig. 2.1.

The reaction vessel was contained in an electrically heated cylindrical coaxial furnace (F_1). This furnace was constructed of two parts, such that they contacted tightly over the centre of the reaction vessel. Each part was separately wired, although electrical contact was made at the junction. It was found that the two parts of the furnace had to be wired in parallel from a variac to obtain the higher temperatures required, and, further, that to maintain a temperature gradient of $\pm$ 2°C along the length of the reaction vessel, it was necessary to have a shunt of 18 ohms across one half of the furnace. The temperature was maintained to $\pm$ 1°C during a run. A thermocouple well extending the entire length of the furnace passed directly under the quartz cell. One end of the furnace contained a quartz window.

The temperature in the reaction vessel was measured by means of a thermocouple constructed from commercial T_1/T_2 wires. The hot junction was placed below the centre of the cell, and the cold junction was maintained at 20°C in a Dewar flask containing water. The potential differences were measured on a Doran potentiometer incorporating a galvanometer. The temperatures were calculated from the T_1/T_2 calibrations supplied by the manufacturers. The glass tubing connected to the reaction vessel and manometer was wound with resistance tape, and could be heated electrically to prevent condensation at high aldehyde pressures.

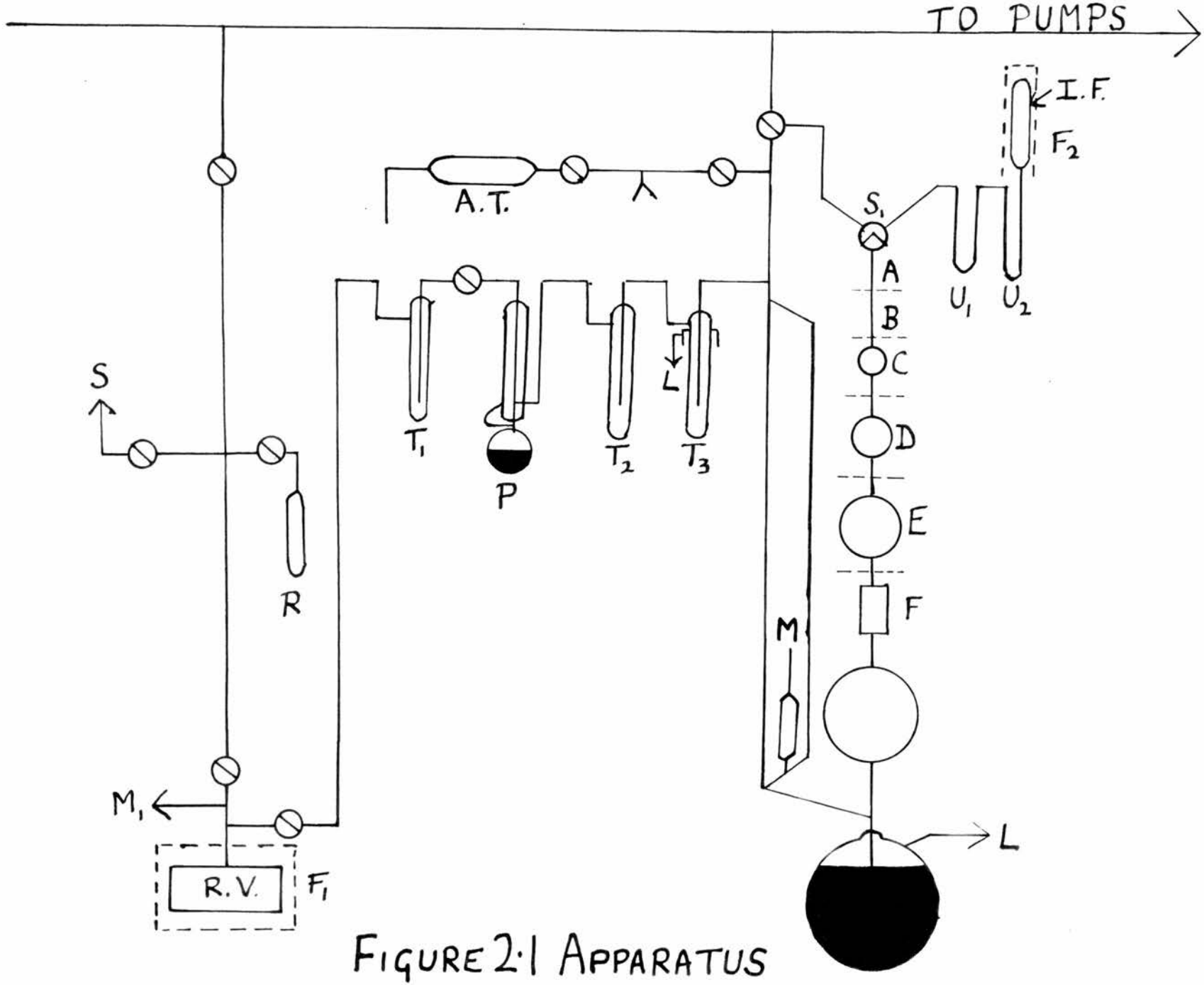


FIGURE 2·1 APPARATUS

The reaction vessel was illuminated by the unfiltered light of a 125 w Osram MB/U medium pressure mercury arc, which was allowed twenty minutes for warming up. The light was rendered parallel by a quartz lens, 10 cm. focal length, and in some runs the intensity was increased by introducing a concave cylindrical aluminium reflector behind the lamp.

The iodine pentoxide tube (I.F.) was housed in a small close-fitting electrically heated furnace (F_2). A thermocouple well was placed along the length of this furnace.

2.2 APPARATUS FOR GAS CHROMATOGRAPHY

A schematic diagram of the chromatographic apparatus is given in Fig. 2.2A. The carrier gas used was hydrogen from a B.O.C. commercial cylinder. The flow was split, passing on the one hand to a mercury bubbler which controlled the pressure head of gas, and on the other hand through a flow regulator. The flow regulator consisted essentially of a U-tube of mercury in parallel with a needle valve. When a high pressure built up behind the needle valve, the mercury, on which a weighted rubber bung floated, rose up to close the outlet. When sufficient pressure built up beyond the needle valve the mercury dropped again, and hydrogen passed through the outlet. In this way a constant flow rate was maintained, even when the resistance of the columns changed due to heating. The flow rate could be adjusted by the needle valve, it was maintained at 30 $cm.^3$ $min.^{-1}$. The carrier gas then passed through a series of buffering vessels, which further stabilised the flow rate. They

were constructed from small tubes joined together by very fine capillary tubing. After this there was a short column of Linde molecular sieve to remove water vapour from the hydrogen.

The carrier gas then passed through the first channel of the conductivity cell. This consisted of a solid brass block through which were drilled two identical channels. Stretched above similar parts of each channel were tungsten filaments of resistance approximately 10 ohms.

The carrier gas was then led through the injection system. This consisted of a W tube which could either be by-passed, while being connected to the high vacuum line, or inserted into the flow. On emerging from the injection system the gas passed through the column. The column was contained in a fibre glass jacket, and lay alongside an electrical heater. Different voltages could be applied to the heater, allowing a variety of temperature programmes. Details of these and column packings will be given in the following chapters.

The emergent gas then passed through the second channel of the conductivity cell, setting up an off-balance current when a hydrocarbon was mixed with the hydrogen. Pure hydrogen always flowed through the first balancing channel of the conductivity cell. The emergent gas then passed through more buffering vessels, and through a butyl phthalate capillary flow meter to the atmosphere. This flow meter was calibrated with a soap bubble flow meter.

The electrical circuit for the conductivity cell is shown in Fig. 2.2B. The voltage for the Wheatstone Bridge circuit was

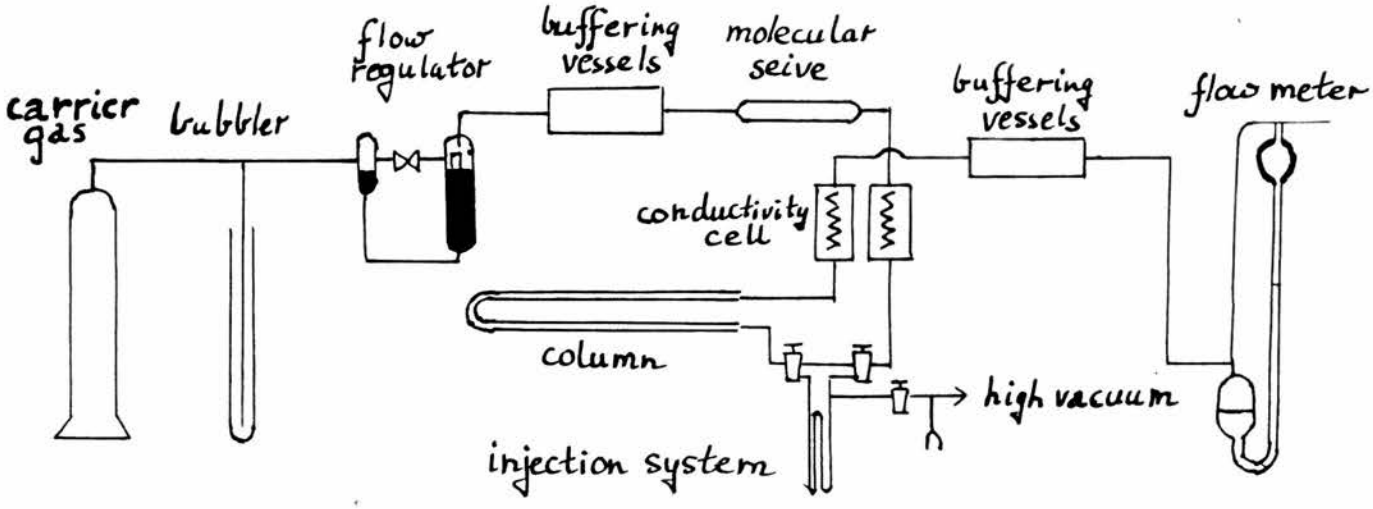


FIGURE 2·2A SCHEMATIC DIAGRAM OF CHROMATOGRAPHY UNIT

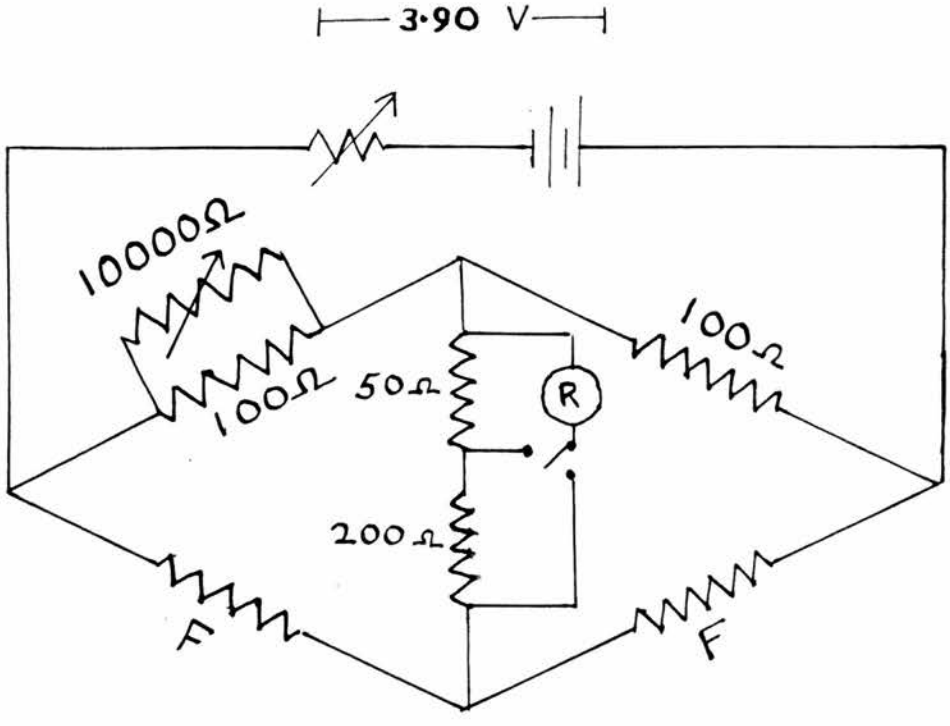


FIGURE 2·2B CIRCUIT FOR CONDUCTIVITY CELL

supplied by two 2 volt accumulators, and was maintained at 3.90 v by means of a 2 ohm rheostat. The filaments (F) in the thermal conductivity gauges formed two arms of the Wheatstone Bridge, and the other two arms consisted of approximately 100 ohm resistances. The 10,000 ohm resistance box across one of these 100 ohm resistances was used to adjust the balance of the bridge. The off-balance current set up when a hydrocarbon passed through the analysing gauge was fed into a 1 m.V. Sunvic recorder, via a voltage divider by which a change of sensitivity of approximately five could be effected.

2.3 CHROMATOGRAPHY CALIBRATIONS

Hydrocarbons from C_2 to C_8 were analysed by the gas chromatography system, and for each gas it was necessary to make a series of calibrations. The procedure consisted of introducing measured volumes of gas at known temperature and pressure, into the injection system of the apparatus. A small gas burette was used for this purpose. It was sealed at one end so that the gas sample would have as little contact as possible with stop-cock grease. The sample was then analysed and a peak obtained on the recorder. The peak area was measured using a planimeter. A calibration graph was then drawn, plotting peak areas against μ moles of gas.

It was found that isomeric hydrocarbons of C_5 and heavier had the same sensitivity within experimental error (2%). Thus samples containing isomers were suitable as calibration samples.

The vapour pressure of octane at room temperature was too low for a satisfactory calibration to be made directly. Thus several

mixtures of 2:3 dimethyl butane/octane of known composition were made up. Small amounts of these mixtures were analysed and the relative sensitivities of the two compounds found. Thus the octane was calibrated indirectly. The sample gases used for calibrations were as follows:

Ethylene, Ethane, Propane, n-Butane and Isobutane were obtained directly from commercial cylinders and were $>$ 98% pure.

Propylene was obtained pure by dehydrating isopropanol with phosphorus pentoxide, and pure Isobutene was obtained by dehydrating t-butanol with concentrated sulphuric acid.

Isopentane, B.D.H., contained other pentanes.

2:3 Dimethyl Butane, L. Light and Co., contained other hexanes.

2:2:4 Trimethyl Pentane, B.D.H., was used in place of 2:5 dimethyl hexane. It also contained some isomers.

It was found that sensitivity, measured in sq. ins. per μ mole, increased with molecular weight. However as the molecular weight increased sensitivity differences between neighbouring homologues became smaller. Olefins were less sensitive than paraffins, but again the difference became unimportant at higher molecular weights.

2.4 EXPERIMENTAL PROCEDURE

The apparatus was pumped down to a pressure of 10^{-5} mm. Hg. or less. The aldehyde or ketone, and any gas to be added were thoroughly degassed. A quantity of aldehyde was introduced into the reaction vessel, and its pressure measured on the manometer. Any gas to be added was then introduced and a second pressure reading

taken. The temperature was noted, and the reaction initiated by removing a shutter placed between the lamp and the window of the furnace. A stop-watch was simultaneously started. Temperature readings were taken at five minute intervals during the run. The reaction was terminated by switching off the lamp, and the watch was simultaneously stopped. The products and unreacted aldehyde were immediately pumped out of the reaction vessel into the low temperature distillation system. Ten minutes with the Toepler pump was usually sufficient to collect the non-condensable gases into the gas burette. When this separation was complete, as indicated on the McLeod gauge, the total amount of non-condensable gases were measured in the gas burette. The non-condensable fraction always contained hydrogen, methane and carbon monoxide in aldehyde photolyses. It was passed into the U tube containing silica gel cooled in liquid oxygen. The uncondensed hydrogen was brought back, measured and pumped off. A correction was applied to allow for the sharing ratio between the gas burette and U tube/iodine pentoxide furnace system. The silica gel was heated in hot water, and the carbon monoxide oxidised in the iodine pentoxide furnace heated to 150°C. Oxidation was facilitated by mixing the gas by raising and lowering the mercury in the gas burette, the process took about twenty minutes. As carbon dioxide was formed it was condensed in U_2 which was cooled with liquid oxygen. The methane was then measured, and the carbon monoxide obtained by difference. In the photolyses of isobutyraldehyde/ethylene mixtures the methane yield was negligible at the temperatures employed, only the total non-condensable fraction and hydrogen were measured in

most runs.

The condensable fraction was distilled three times in either direction through the aldehyde absorbent in the tube (A.T.), condensing the sample on a cold finger each time. The gases not absorbed were then condensed into a tapped sample tube, and subsequently distilled into the injection system of the chromatographic unit and analysed.

SPECIMEN RUN (Photolysis of Isovaleraldehyde)

Run No. 40. Isovaleraldehyde pressure = 43.7 mm.
Initial [Isovaleraldehyde] = 1.27×10^{-6} moles. $cm.^{-3}$
Length of run = 900 secs.

Time	0 min.	5 min.	10 min.	15 min.	Mean
Cold Junction	21.64°C	21.65	21.63	21.65	21.64
Hot Junction	10.45 mv	10.45	10.49	10.50	10.47

Hence furnace temperature = 552.1 °A

Analysis of non-condensable gases - gas burette

Product	Gas burette reading	Volume of burette	Pressure in burette (cm.)	μmoles of product	corrected amount*	Rate of formation 10^{-12} moles. $cm.^{-3}$ $sec.^{-1}$
Total	39.38	A + B + C	17.92	37.82	-	-
H_2	36.10	A + B	10.66	1.67	1.84	11.6
CH_4	24.41	A + B + C	-	-	-	-
	24.12	A + B + C	-	-	-	-
	24.00	A + B + C	2.60	5.57	6.13	38.5
CO	-	-	-	-	29.85	187

* This correction is for the gas burette/I_2O_5 furnace sharing ratio.

Analysis of condensable gases - gas chromatography

Product	Peak Area (sq.in.)	μmoles product	Rate of formation 10^{-12} mole. $cm.^{-3}$ $sec.^{-1}$
Propylene	0.39	10.9	68.4
Isobutane	1.85	41.6	261
Isobutene	0.27	1.10	6.91

Calculation of mean Isovaleraldehyde

Length of run	R_{CO} 10^{-12} mole. $cm.^{-3}$ $sec.^{-1}$	[CO] 10-6moles. $cm.^{-3}$	Initial [Ald.] 10^{-6}moles. $cm.^{-3}$	Final [Ald.] 10^{-6}moles. $cm.^{-3}$	Mean [Ald.] 10^{-6}moles. $cm.^{-3}$	% Decomp.
900 secs.	187	0.169	1.270	1.101	1.19	13.3

2.5 MODIFICATIONS TO APPARATUS AND PROCEDURE IN ISOPROPYL COMBINATION WORK

Intermittent illumination was produced by regularly chopping the light beam with a rotating disc from which two slots had been cut to give a dark:light ratio of 3:1. The disc was driven by an Eversheed and Vignoles D.C. Servo motor. Fig. 2.5A shows the circuit diagram for the motor. The speed could be varied by adjustment of the 500 ohm rheostat. The fixed resistance of 100 ohms limited the current to 1 amp. The motor was fitted with a tacho generator, this generated approximately 21 volts when the sector was rotating at 1000 rev. per minute. The voltage was measured by a double range 0-20 v, 0-50 v, British Physical Laboratories voltmeter. The tacho generator/voltmeter was calibrated using a Dawe Instrument Co. Strobflash. Speeds of rotation between 100 and 2000 rev. per minute could be achieved by the motor, very slow flashing speeds were obtained by rotating the sector manually.

The light source was an 80 W Osram MB/U medium pressure mercury arc, at full intensity the arc width was about 2 mm. This was mounted behind a narrow slit immediately behind the rotating sector, so that a very narrow beam was chopped. The sector width:slit width was 20:1, however this is a conservative estimate of the sector width: beam width, so penumbra effects should be negligible. The arrangement of the light and sector is shown schematically in Fig. 2.5B. The lamp was protected from draught by a quartz window and metal shield. The beam was rendered parallel by a 10 cm. quartz lens placed at the focal distance from the sector, incorporated in the

furnace wall in front of the reaction vessel. An estimate slightly below 10 cm. was made for the focal length of the lens, with reference to ultra violet light.

A stabilised D.C. voltage supply was used for the lamp. Fig. 2.5C shows the circuit diagram of the lamp. 230 V A.C. current was fed into an Advance 125 W constant voltage transformer (C.V.T.) to stabilise mains fluctuations. The output voltage was then transformed by a variac and rectified by a Powerpak, incorporating four selenium rectifiers. The amperage and voltage supplied to the lamp could be adjusted by means of the variac and the 245 ohm rheostat (R) in series with the lamp. The amperage and potential difference across the lamp were monitored using a 1 amp ammeter and a 150 V voltmeter.

Before the arc was struck the rheostat R was adjusted to about 100 ohms. Then the output voltage of the variac was gradually raised, till at about 175-200 volts the arc was struck. Immediately the voltage from the variac was lowered so that the current through the lamp did not exceed 1 amp. As the lamp warmed up the current fell and the voltage rose. Gradually the rheostat R was reduced to about 20 ohms and the variac output voltage raised, while keeping the current below 1 amp. The specifications of the lamp were such that it tended to stabilise at a certain voltage, which depended on its rate of cooling. In practice it ran at about 108 volts and 0.65 amps. Small adjustments from run to run could be made with the variac and rheostat R. After final adjustments had been made the lamp was allowed twenty minutes to stabilise before the reaction was commenced.

The furnace was maintained at constant temperature for long periods using a Sunvic R.T.2 thermoregulator. The detecting element was a platinum resistance thermometer placed inside the furnace parallel to thermocouple well. This formed one arm of the Wheatstone Bridge circuit of the thermoregulator. The thermoregulator operated on the principle of proportional control, alternately switching the current through the furnace and the low resistance of the thermoregulator, and through the furnace and an increment resistance of 22 ohms, 30% of the furnace resistance, in series with the furnace. The temperature was constant within $\pm$ 0.7°C for long periods.

Before a run was commenced the speed of rotation of the sector was allowed to stabilise. This took up to 30 minutes depending upon the speed. The temperature, speed of rotation, and amperage and potential difference across the lamp were noted at five minute intervals.

In runs in which ethylene was added in large amounts, the traps T_1, T_2 and T_3 were cooled with liquid nitrogen. After the non-condensables had been removed, the contents of T_1 were allowed to evaporate to T_2 and T_3. Any non-condensable gas which had been frozen out with the ethylene was freed and pumped off. In other respects the apparatus and procedure was similar to that used in the photolysis of isovaleraldehyde.

FIG. 2·5A SECTOR MOTOR CIRCUIT

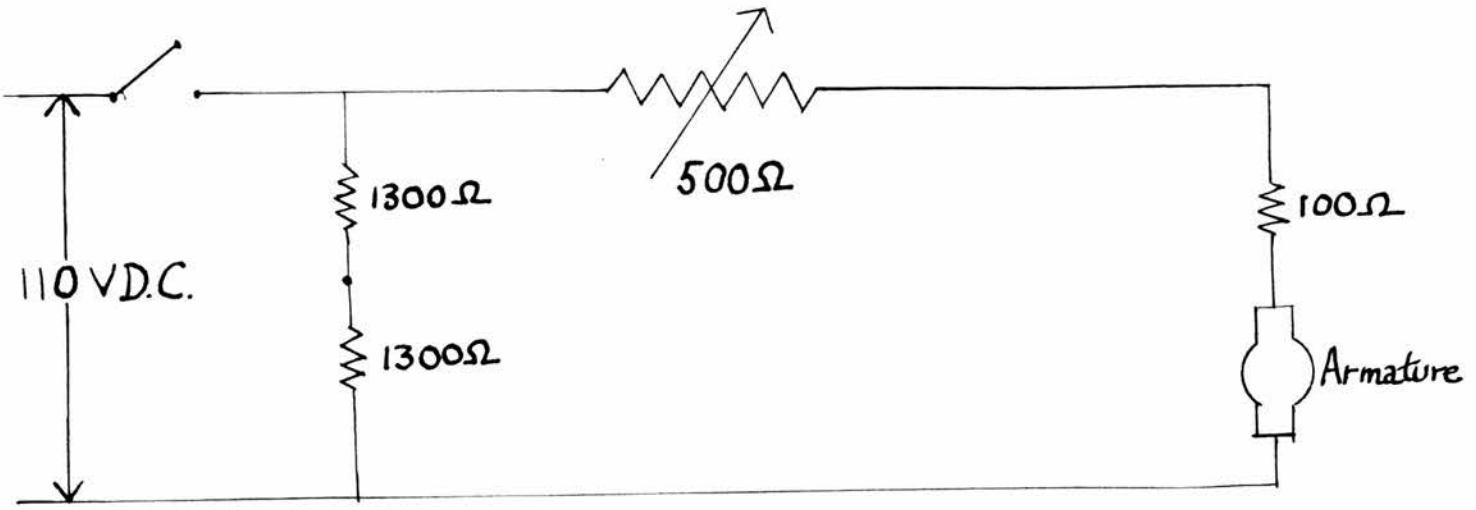


FIG. 2·5B CROSS-SECTION OF ILLUMINATION OF REACTION VESSEL

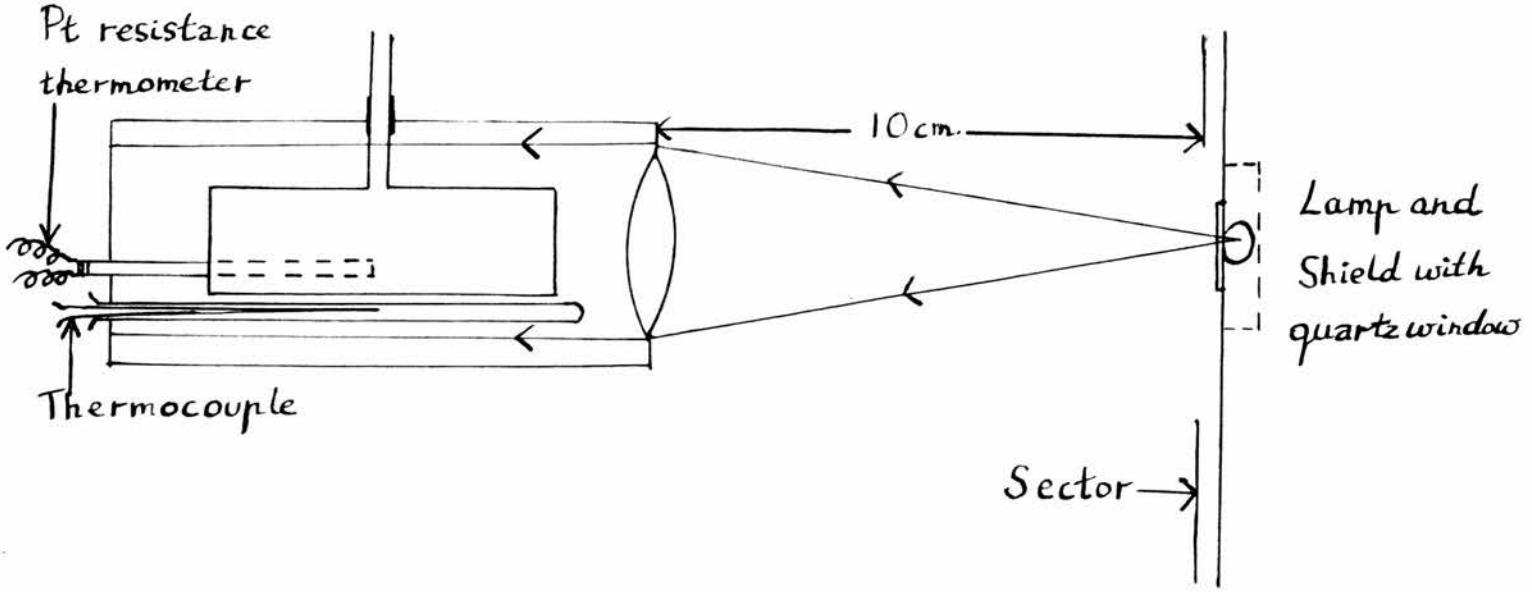
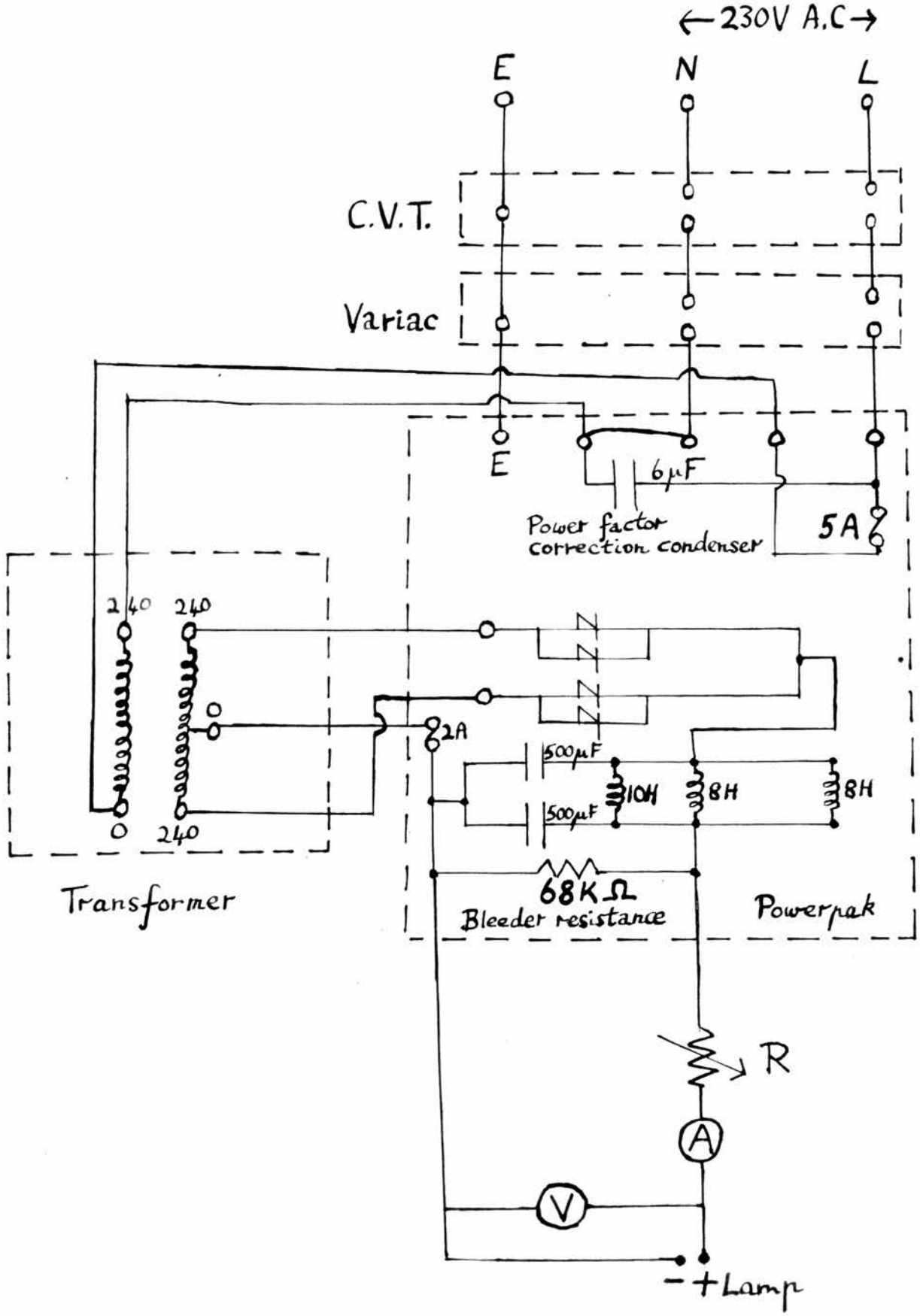


FIGURE 2·5C LAMP CIRCUIT



SPECIMEN RUN (Photolysis of Isobutyraldehyde/Ethylene)

Run No. 48. Isobutyraldehyde pressure = 35.5 mm.
Initial [Isobutyraldehyde] = 1.29×10^{-6} moles. $cm.^{-3}$
Ethylene pressure = 30.9 mm.
Initial [Ethylene] = 1.12×10^{-6} moles. $cm.^{-3}$
Length of run = 1800 secs.

Time	0 minutes	5	10	15	20	25	30	Mean
Cold Junction	19.67°C	19.67	19.67	19.67	19.69	19.69	19.70	19.68
Hot Junction	6.12 mv	6.11	6.11	6.11	6.12	6.11	6.11	6.11
Tacho voltmeter	8.50 volts	8.55	8.65	8.62	8.55	8.45	8.25	8.51
Lamp current	0.659 amps	0.658	0.653	0.648	0.648	0.647	0.647	0.651
Lamp voltage	107.8 volts	108.2	108.7	109.1	109.2	109.3	109.1	108.8

Furnace temperature = 442.5 °A
Power of lamp = 70.8 watts
Mean sector speed = 405.2 r.p.m.
Log length light flash = $\bar{2}.267$
Corrected log length light flash = $\bar{2}.303$
(This correction is for the calibration of the tachometer/voltmeter.)

Analysis of total non-condensables and hydrogen, and of condensable fraction as for isovaleraldehyde photolysis

Calculation of Mean [Ethylene]

Length of run	$R_{C_5H_{12}}$ 10^{-12} mole. $cm.^{-3} sec.^{-1}$	$[C_5H_{12}]$ 10^{-6} mole. $cm.^{-3}$	Initial $[C_2H_4]$ 10^{-6} mole. $cm.^{-3}$	Final $[C_2H_4]$ 10^{-6} mole. $cm.^{-3}$	Mean $[C_2H_4]$ 10^{-6} mole. $cm.^{-3}$
1800 secs.	7.30	0.013	1.120	1.107	1.114

CHAPTER III

ISOBUTYL RADICALS FROM THE PHOTOLYSIS OF ISOVALERALDEHYDE

Summary. The photo-initiated chain decomposition of isovaleraldehyde has been studied, and a mechanism accounting for the rates of formation of the principal products constructed. On the assumption that the rate constant for the combination of isobutyl radicals is given by log k (mole.$^{-1}$ cm.^{3} sec.$^{-1}$) = 14, the following Arrhenius parameters of the principal rate-determining reactions have been found (A in mole.$^{-1}$ cm.^{3} sec.$^{-1}$ or sec.$^{-1}$; E in k. cal. mole.$^{-1}$):

	log A	E
$2\ C_4H_9 = C_4H_8 + C_4H_{10}$	13.21	0
$C_4H_9 + C_4H_9CHO = C_4H_{10} + C_4H_9CO$	11.7	6.5
$C_4H_9 + C_4H_9CHO = C_4H_{10} + C_4H_8CHO$	12.7	12.6
$C_4H_9 = CH_3 + C_3H_6$	12.8	26.2
$C_4H_9 = H + C_4H_8$	13.0	30.7

A comparison of isobutyl with other alkyl radicals is to be found in the appropriate sections of Chapter I.

3.1 EXPERIMENTAL

The apparatus and procedure were as described in Sections 2.1 - 2.4. Isovaleraldehyde, L. Light and Co., was shown to be pure by gas chromatography. The condensable fraction of the products was analysed on a column (135 x 0.5 cm.) packed with 3% dinonyl

phthalate/60-90 mesh activated alumina, which was heated during the analysis and rose from 20°C to 140°C in 70 minutes.

3.2 RESULTS AND DISCUSSION

Table 3 records the conditions, products, and rate constants derived from the runs. These results show that all the reactions listed below occur during the photolysis. Deductions can be made about the rate constants of the reactions designated by a simple number.

$$(CH_3)_2CH\ CH_2CHO + h\nu \begin{cases} \longrightarrow (CH_3)_2CH\ CH_2 + CHO & (a) \\ \longrightarrow (CH_3)_3CH + CO & (b) \\ \longrightarrow C_3H_6 + CH_3CHO & (c) \\ \longrightarrow C_3H_6 + CH_3 + CHO & (d) \end{cases}$$

$$2\ C_4H_9 \xrightarrow{k_1} C_8H_{18} \quad (1)$$

$$2\ C_4H_9 \xrightarrow{k_2} C_4H_{10} + C_4H_8 \quad (2)$$

$$C_4H_9 + C_4H_9CHO \xrightarrow{k_3} C_4H_{10} + C_4H_9CO \quad (3)$$

$$C_4H_9CO \longrightarrow C_4H_9 + CO \quad (3a)$$

$$C_4H_9 + C_4H_9CHO \xrightarrow{k_4} C_4H_{10} + C_4H_8CHO \quad (4)$$

$$C_4H_8CHO \longrightarrow C_4H_8 + CHO \quad (4a)$$

$$CHO + C_4H_9CHO \longrightarrow H_2CO + C_4H_9CO \quad (4b)$$

$$CHO \longrightarrow H + CO \quad (4c)$$

$$H + C_4H_9CHO \longrightarrow H_2 + C_4H_9CO \quad (4d)$$

$$C_4H_9 \xrightarrow{k_5} CH_3 + C_3H_6 \quad (5)$$

$$CH_3 + C_4H_9CHO \longrightarrow CH_4 + C_4H_9CO \quad (5a)$$

$$2\ CH_3 \longrightarrow C_2H_6 \quad (5b)$$

$$C_4H_9 \xrightarrow{k_6} H + C_4H_8 \quad (6)$$

The Photolytic Act (a), (b), (c), and (d). The primary process in the photolysis of isovaleraldehyde has not been fully investigated though Bamford and Norrish[155] showed that both (a) and (b) occurred. The present work does not give quantitative data about the processes, but the results show that they all occur. At low temperatures the rate of production of isobutane is roughly constant; it is presumably produced by (b). The rate of production of propylene, when corrected to unit aldehyde concentration and unit light intensity, as measured by octane formation, is roughly constant from 26°C to 206°C; it is produced by (c), or possibly by (d). The runs below 70°C show that (c) or (d) account for about 60% of the decomposition of the aldehyde. This type of primary process is well known in the photolysis of any aldehyde or ketone with a straight side-chain of three or more carbon atoms, examples are given in Section 1.1. The process will increase in importance as the number of γ-hydrogen atoms increases, because a γ-hydrogen atom is transferred to the α-carbon atom as the bond between the α- and the β-carbon atom breaks. Process (c) occurs in the photolyses of n-butyraldehyde,[30] n-valeraldehyde,[32] and 1-methyl butyraldehyde[29] and is most important for isovaleraldehyde which has six γ-hydrogen atoms. Process (d) is postulated as well as (c) because there is a small constant rate of methane formation at low temperatures. It is unlikely that all the methane is a secondary product from the photolysis of acetaldehyde formed by (c).

Combination of Isobutyl Radicals (1). This reaction is the source of 2:5, dimethyl hexane in the products, which is formed

according to the equation:

$$R_{C_8H_{18}} = k_1 [C_4H_9]^2$$

This rate constant, k_1, has never been measured; for the purpose of the description of the experimental results, it has been assumed that $k_1 = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$.

Disproportionation of Isobutyl Radicals (2). Twelve runs that provide direct information on k_2 were carried out between 26°C and 124°C with concentrations of aldehyde between 1 and 2 x 10^{-6} moles. cm.$^{-3}$. Direct comparison of the rates of formation of isobutene and the octane gave the disproportionation-combination ratio:

$$k_2/k_1 = R_{C_4H_8}/R_{C_8H_{18}}$$

The logarithms of this ratio are plotted against the reciprocal of the absolute temperature in Fig. 3. The results, calculated by the least-squares method, give $E_2 - E_1 = 0$ and $A_2 = 0.165\ A_1$. Therefore

$$\log k_2 \text{ (mole.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}) = 13.21 \pm 0.03$$

All errors quoted are 50% confidence errors.

The value of 0.165 does not agree with that found by Kraus and Calvert[10] from the photolysis of di-isobutyl ketone. Their value is probably too high because isobutene can be produced both by disproportionation and by the decomposition of the radical formed when isobutyl abstracts hydrogen from its parent ketone.

If $k_2/k_1 = 0.42$, then their results yield by least squares

$$\log k_7 (\text{mole.}^{-1} \text{cm.}^3 \text{sec.}^{-1}) = (11.40 \pm 0.20) - (7560 \pm 360)/2.3RT$$

for the abstraction reaction (7).

$$C_4H_9 + C_4H_9COC_4H_9 \xrightarrow{k_7} C_4H_{10} + C_4H_9COC_4H_8 \qquad (7)$$

If the value of $k_2/k_1 = 0.165$ found in this work is used in the recalculation of Kraus and Calvert's results, then

$$\log k_7(\text{mole.}^{-1}\text{cm.}^3\text{sec.}^{-1}) = (11.06 \pm 0.09) - (6830 \pm 160)/2.3RT$$

Thus the errors are halved by the adoption of the lower value of k_2/k_1. It is impossible to derive an accurate value of k_2/k_1 from Kraus and Calvert's work but their results are compatible with the value obtained here.

Abstraction of Hydrogen Atoms from Isovaleraldehyde (4). This abstraction reaction is conveniently considered before reaction (3), although it only occurs measurably at higher temperatures than (3). Above 178°C the rate of formation of isobutene rose sharply. The temperature is too low for the decomposition of the isobutyl radical. The extra isobutene can be accounted for by reaction (4) followed by (4a). Hence,

$$C_4H_8 \text{ (reaction 4a)} = C_4H_8 \text{ (total)} - C_4H_8 \text{ (reaction 2)}$$
$$= C_4H_8 \text{ (total)} - 0.165\ C_8H_{18}$$

where the reactions noted in parentheses are those by which the products are formed. Therefore,

$$R_{C_4H_{10}} \text{ (reaction 4)} = R_{C_4H_8} \text{ (reaction 4a)} = k_4\left[C_4H_9\right]\left[C_4H_9CHO\right]$$

and

$$k_4/k_1^{\frac{1}{2}} = R_{C_4H_8} \text{ (reaction 4a)}/R_{C_8H_{18}}^{\frac{1}{2}}\left[C_4H_9CHO\right]$$

The values of this ratio between 178°C and 307°C, plotted in Fig. 3, and calculated by the least-squares method, yield

$$\log k_4(\text{mole.}^{-1}\text{cm.}^3\text{sec.}^{-1}) = (12.62 \pm 0.05) - (12{,}700 \pm 200)/2.3RT$$

The runs at 307° were neglected in this calculation because some isobutene may be produced by reaction (6) at this temperature.

Reactions (4c) and (4d) are postulated because the rate of hydrogen production increased with that of isobutene. Reaction (4b) is suggested because it is known to follow the reaction analagous to (4) in the photolyses of n-butyraldehyde,[30] isobutyraldehyde,[31] and pivalaldehyde,[34] but it is less certain in the case of isovaleraldehyde because the rate of hydrogen production always exceeded that of isobutene. It is probable that the hydrogen atom abstracted in reaction (4) is the tertiary atom, because the radical thereby produced can form isobutene directly, also this is the weakest C-H bond in the alkyl group.

Abstraction of Hydrogen Atoms from Isovaleraldehyde (3).

According to the mechanism, the rate of attack of isobutyl on the carbonyl hydrogen atom in isovaleraldehyde can be taken as

$$R_{C_4H_{10}} - R_{C_4H_8}\,(2) - R_{C_4H_8}\,(4a)$$

Hence $$k_3/k_1^{\frac{1}{2}} = R_{C_4H_{10}} - R_{C_4H_8}/R_{C_8H_{18}}{}^{\frac{1}{2}}\left[C_4H_9CHO\right]$$

At the temperatures considered no isobutene was produced by decomposition of isobutyl, so

$$R_{C_4H_8}\,(\text{total}) = R_{C_4H_8}\,(2) + R_{C_4H_8}\,(4a)$$

$k_3/k_1^{\frac{1}{2}}$ was determined in 19 runs between 117°C and 230°C at aldehyde concentrations between 0.7 and 3.1 x 10^{-6} moles. cm.$^{-3}$. The results, plotted in Fig. 3 and calculated by the least-squares method, yield

$$\log. k_3(\text{mole.}^{-1}\text{cm.}^3\text{sec.}^{-1}) = (11.71 \pm 0.07) - (6500 \pm 100)/2.3RT$$

The variation in aldehyde concentration and a change in light intensity produced by the use of the reflector in some runs did not affect the rate constants. A series of five consecutive runs in which log $k_3/k_1^{\frac{1}{2}}$ was uniformly slightly high has been rejected: an impurity was probably present in the aldehyde, because a fresh sample yielded normal rate constants. The Arrhenius parameters for this abstraction reaction agree fairly well with those of other alkyl radicals; also log k_3 at 182° is similar to the other abstraction rate constants.

Decomposition of Isobutyl to Propylene (5). Above 279°C the rate of formation of propylene rose sharply. This was attributed to reaction (5) and hence,

$$k_5/k_1^{\frac{1}{2}} = \left\{R_{C_3H_6}\ (\text{total}) - R_{C_3H_6}\ (\text{initial act})\right\} / R_{C_8H_{18}}^{\frac{1}{2}}$$

For 25 runs below 206°C the rate of propylene production, corrected to unit aldehyde concentration and unit light intensity by dividing by $\frac{1}{2}R_{C_8H_{18}}$, varied between 11.4 and 34.4 x 10^{-12} moles. cm.$^{-3}$ sec.$^{-1}$. On average $R_{C_3H_6}$ (initial act)/$\left[C_4H_9CHO\right] R_{C_8H_{18}}$ = 9.5.

This correction was applied in the calculation of k_5. At the lowest temperature at which k_5 was determined the propylene from the initial act was 40% of the total, but at the highest temperature it contributed less than 1% to the total propylene.

At these temperatures the runs were short and the amount of octane produced was too small to be measured; it was therefore calculated from $R_{C_4H_{10}}$, k_1, k_3 and k_4. Eight runs between 279°C and 417°C are plotted in Fig. 3, and the results, calculated by the

least-squares method, give

$$\log k_5(\text{sec.}^{-1}) = (12.82 \pm 0.08) - (26{,}200 \pm 300)/2.3RT.$$

Similarly, from the mechanism,

$$k_5/k_1^{\frac{1}{2}} = (R_{CH_4} + 2R_{C_2H_6})/R_{C_8H_{18}}^{\frac{1}{2}}$$

Even at the highest temperatures the amount of ethane produced was very small, and was neglected. Isopentane from the combination of methyl and isobutyl was also negligible. The results, calculated by least squares from the rate of methane production, give

$$\log k_5(\text{sec.}^{-1}) = (12.36 \pm 0.31) - (24{,}700 \pm 1100)/2.3RT.$$

The results calculated on methane show less precision than those calculated on propylene, but they almost agree within experimental error.

The activation energy for this decomposition is close to the heat of reaction, and so has probably been underestimated by about 6 k. cal. mole.$^{-1}$, the activation energy of the reverse addition.[121] A possible source of error is the high temperature formation of extra isobutane, by hydrogen abstraction from the alkyl group. Reaction (4) probably only measures abstraction of the tertiary hydrogen, at high temperatures abstraction will be less discriminative.

Decomposition of Isobutyl to Isobutene (6). Above 329°C the rate of formation of isobutene rose sharply and could no longer be accounted for by reactions (4) and (4a). This was attributed to reaction (6), and hence

$$k_6/k_1^{\frac{1}{2}} = \left\{R_{C_4H_8} - R_{C_4H_8}\ (\text{reaction 4a}) - R_{C_4H_8}\ (\text{reaction 2})\right\}/R_{C_8H_{18}}^{\frac{1}{2}}$$

or

$$k_6/k_1^{\frac{1}{2}} = R_{H_2}/R_{C_8H_{18}}^{\frac{1}{2}}$$

The rate of octane formation was again calculated from $R_{C_4H_{10}}$, k_1, k_3 and k_4. The isobutene from reaction (4a) was calculated; that from reaction (2) was negligible. Five runs between 329°C and 417°C at aldehyde concentrations of about 0.9×10^{-6} mole. cm.$^{-3}$ are shown in Fig. 3, and yield

$$\log k_6(\text{sec.}^{-1}) = 13.0 - (30{,}700/2.3RT)$$

The rate constants calculated on the rate of production of hydrogen were very scattered but in each case gave higher values than those calculated on the isobutene production. It is believed that the hydrogen analyses were unreliable, because it is difficult to determine small amounts of hydrogen in the presence of large amounts of carbon monoxide and methane.

The activation energy is lower than the heat of reaction, and so has been underestimated in common with other similar decompositions studied by aldehyde photolyses.[30,31,33,34] The same error as was suggested in reaction (5) may apply.

The A factors for both decompositions should be 10^{13} sec.$^{-1}$, if the entropies of the radicals and the A factors for the addition reactions are assumed to be normal. In both cases the experimental A factors are close to this value.

Key to Figure 3

Arrhenius plots for the reactions of isobutyl: (2) disproportionation, k_2/k_1, scales at top right-hand corner refer to this reaction; (3) hydrogen abstraction, $k_3/k_1^{\frac{1}{2}}$ (mole.$^{-\frac{1}{2}}$ cm.$^{3/2}$ sec.$^{-\frac{1}{2}}$); (4) hydrogen abstraction from alkyl group, $k_4/k_1^{\frac{1}{2}}$ (mole.$^{-\frac{1}{2}}$ cm.$^{3/2}$ sec.$^{-\frac{1}{2}}$); (5) decomposition to methyl and propylene, $10^6\ k_5/k_1^{\frac{1}{2}}$ (mole.$^{-\frac{1}{2}}$ cm.$^{-3/2}$ sec.$^{-\frac{1}{2}}$) - open circles, results based on propylene; filled circles results based on methane (which are displaced upwards by 0.4 log unit); (6) decomposition to hydrogen and isobutene, $10^6\ k_6/k_1^{\frac{1}{2}}$ (mole.$^{-\frac{1}{2}}$ cm.$^{-3/2}$ sec.$^{-\frac{1}{2}}$).

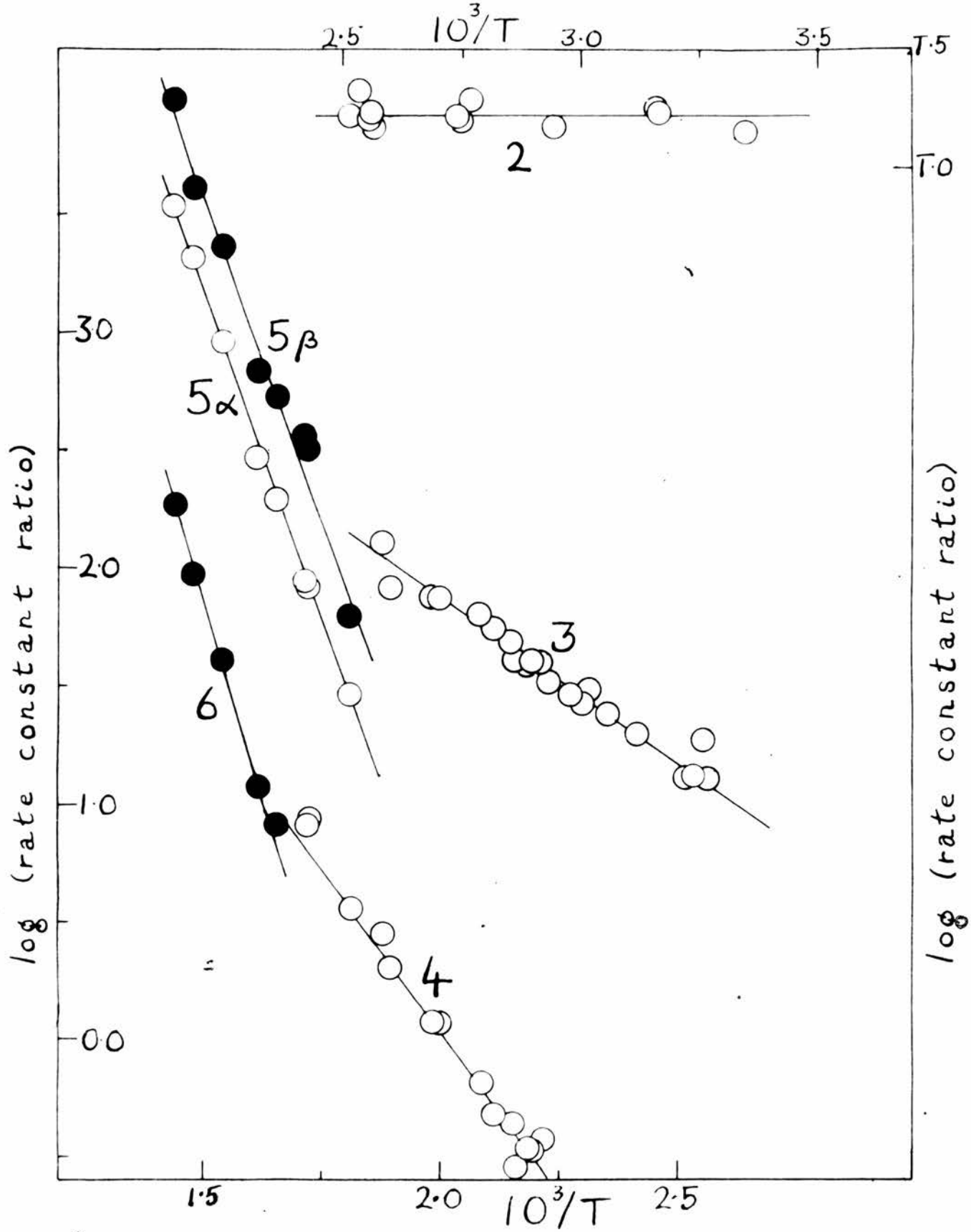

2·5
10³/T
3·0
3·5
T·5
T·0
2
5β
5α
3
6
4
3·0
2·0
1·0
0·0
log (rate constant ratio)
1·5
2·0
10³/T
2·5

FIGURE 3

Notes on Table 3

All products are in rates of formation of 10^{-12} mole. cm.$^{-3}$ sec.$^{-1}$ and all subsequent calculations involve these units.

[Ald.] is the mean concentration of aldehyde, in 10^{-6} mole. cm.$^{-3}$.

$k_3/k_1^{\frac{1}{2}}$ and $k_4/k_1^{\frac{1}{2}}$ are in mole.$^{-\frac{1}{2}}$ cm.$^{3/2}$ sec.$^{-\frac{1}{2}}$;

$k_5/k_1^{\frac{1}{2}}$ and $k_6/k_1^{\frac{1}{2}}$ are in 10^6 mole.$^{-\frac{1}{2}}$ cm.$^{-3/2}$ sec.$^{-\frac{1}{2}}$.

C_4H_{10} - Isobutane.

C_4H_8 = Isobutene.

C_8H_{18} - 2:5,Dimethyl hexane.

* Calculated value.

a.f. = analytical failure.

R = reflector present.

TABLE 3 PHOTOLYSIS OF ISOVALERALDEHYDE

RUN No.	TEMP. ^{o}C	TIME (sec.)	[ALD]	CO	H_2	CH_4	C_3H_6
21 R	25.7	12,000	1.14	18.4	2.69	3.80	12.6
19 R	47.0	9,600	1.46	21.4	3.30	3.99	29.7
20 R	47.8	8,400	1.74	30.4	2.39	2.33	37.7
18	66.8	10,800	2.02	21.1	2.30	4.64	27.3
16	86.9	10,800	0.972	10.6	0.829	2.15	11.8
17	90.6	8,100	1.22	14.2	0.858	3.22	25.6
15	92.9	11,533	1.25	11.6	1.02	2.93	14.1
4	117.0	9,600	1.57	14.8	0.788	4.96	18.5
5	117.9	7,200	1.77	21.0	0.926	0.918	a.f.
3	118.2	7,041	1.47	20.8	0.963	2.63	22.9
1	121.1	10,218	1.48	21.4	1.16	10.7	13.9
2	123.9	11,455	1.23	12.6	1.11	17.3	13.2
14	141.3	7,300	1.57	15.0	0.672	2.89	9.67
13	151.6	4,800	1.87	22.8	0.985	2.50	15.6
34	158.5	1,800	1.59	41.8	3.11	4.74	29.0
22 R	161.2	1,200	2.77	110	7.61	25.5	71.8
23 R	165.7	4,200	0.675	18.0	2.96	2.96	19.5
33	175.6	1,800	1.74	69.6	4.08	4.08	27.0
8	178.4	3,664	1.35	31.2	3.22	3.38	12.3
7	182.6	3,600	1.47	45.6	2.83	1.82	18.8
6	184.4	3,707	1.27	38.2	2.20	1.92	12.2
35	190.1	1,500	1.34	58.5	4.04	6.57	20.7
37 R	191.7	1,800	1.06	59.7	5.19	3.64	26.2
31	200.1	2,400	1.43	93.3	10.3	7.58	30.6
32	205.7	1,800	1.73	95.5	9.54	13.9	31.4

C_4H_{10}	C_4H_8	C_8H_{18}	k_2/k_1	$k_3/k_1^{\frac{1}{2}}$	$k_4/k_1^{\frac{1}{2}}$	$k_5/k_1^{\frac{1}{2}}$	$k_6/k_1^{\frac{1}{2}}$
5.18	0.129	0.920	0.140	-	-	-	-
17.1	0.382	2.26	0.169	-	-	-	-
21.9	0.504	2.84	0.178	-	-	-	-
22.8	0.319	2.15	0.149	-	-	-	-
9.89	0.136	0.709	0.192	-	-	-	-
18.0	0.195	1.26	0.155	-	-	-	-
16.7	0.200	1.21	0.165	-	-	-	-
26.7	0.227	1.77	0.128	12.7	-	-	-
a.f.	0.243	1.43	0.170	-	-	-	-
33.7	0.233	1.46	0.159	18.8	-	-	-
20.4	0.227	1.08	0.210	13.1	-	-	-
20.4	0.261	1.57	0.166	13.0	-	-	-
26.6	0.225	0.727	-	19.7	-	-	-
39.9	0.188	0.777	-	24.1	-	-	-
66.2	0.439	1.85	-	30.4	-	-	-
198	1.16	7.27	-	26.4	-	-	-
26.4	0.323	1.76	-	29.1	-	-	-
82.2	0.690	2.07	-	32.7	-	-	-
51.6	0.632	0.910	-	39.5	0.374	-	-
70.3	0.816	1.41	-	39.8	0.334	-	-
57.9	0.731	1.37	-	38.5	0.340	-	-
70.0	0.753	1.62	-	40.6	0.285	-	-
83.1	1.16	2.55	-	49.0	0.435	-	-
116	1.34	2.12	-	55.2	0.479	-	-
150	1.66	1.79	-	64.1	0.647	-	-

TABLE 3 (continued)

RUN No.	TEMP. ^{o}C	TIME (sec.)	[ALD]	CO	H_2	CH_4	C_3H_6
12	226.2	2,700	1.12	29.6	4.23	8.26	9.10
11	230.3	2,444	0.938	25.0	2.47	9.47	8.67
10	253.9	1,201	1.12	93.2	5.13	8.60	24.7
9	258.4	1,200	1.21	86.2	5.32	18.7	33.0
40	278.9	900	1.19	187	11.6	38.5	68.4
38	306.1	720	0.957	123	12.4	154	112
39	307.5	900	1.17	182	35.7	182	132
43	329.0	420	0.954	297	27.2	270	262
42	344.7	480	0.659	294	29.5	292	324
44	373.3	360	0.983	379	62.7	699	681
45	401.4	240	1.03	895	218	920	1153
46	417.6	120	1.14	858	135	2328	2057

C_4H_{10}	C_4H_8	C_8H_{18}	k_2/k_1	$k_3/k_1^{\frac{1}{2}}$	$k_4/k_1^{\frac{1}{2}}$	$k_5/k_1^{\frac{1}{2}}$	$k_6/k_1^{\frac{1}{2}}$
52.1	0.858	0.377	-	74.8	1.16	-	-
49.9	0.855	0.485	-	75.1	1.19	-	-
106	2.68	1.22	-	83.1	2.00	-	-
135	3.06	0.753	-	126	2.81	-	-
261	6.91	2.34 *	-	-	3.61	27.6	-
224	10.2	1.42 *	-	-	8.74	83.0	-
291	12.4	1.59 *	-	-	8.24	90.4	-
291	21.7	1.60 *	-	-	-	196	8.08
198	21.8	1.18 *	-	-	-	292	11.9
257	44.6	0.547*	-	-	-	914	40.8
250	70.4	0.304*	-	-	-	2085	97.5
341	138	0.361*	-	-	-	3418	187

CHAPTER IV

THE ABSOLUTE RATE OF ISOPROPYL COMBINATION

Summary. The absolute combination rate of isopropyl has been determined between 81°C and 169°C, using intermittent illumination. The radicals were generated by the photo-initiated chain decomposition of isobutyraldehyde. Addition of isopropyl to ethylene was used to measure the relative radical concentration. The activation energy is zero within experimental error, and the A factor is $10^{13.8}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$. A first-order termination correction was applied.

4.1 INTRODUCTION

Kerr and Trotman-Dickenson[31] have studied the reactions of isopropyl from the photo-initiated chain decomposition of isobutyraldehyde. The experimental rate constants were expressed relative to the usual assumed combination rate constant, $k_1 = 10^{14}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$. There is a lack of absolute rate constants for higher alkyl radicals. Isopropyl was chosen for the present study because it is an example of a secondary radical, and also because the primary photolytic act, in which it is formed, is relatively clean.

The theory of intermittent illumination can be applied to any system in which radicals are mutually destroyed in pairs.

e.g. $M + h\upsilon \longrightarrow R$ Initiation

$R + M^1 \longrightarrow R$ Chain

$2R \longrightarrow$ Inactive products Termination

The radical concentration then depends upon the square root of the light intensity. A full treatment of the theory including necessary data is given by Melville and Burnett.[38] They deduce the variation of $[\text{rad.}]_i / [\text{rad.}]_s$ with log m, where $[\text{rad.}]$ = radical concentration, and the subscripts, i and s, refer to intermittent and steady illumination, m is a dimensionless parameter defined by:

$$m = (I_n k_t)^{\frac{1}{2}} \lambda \qquad (I)$$

where I_n = Rate of initiation

k_t = termination rate constant

λ = length of light flash.

It is also shown that $m = \lambda / \tau_s$ (II)

where τ_s = mean radical lifetime under steady conditions. The variation of $[\text{rad.}]_i / [\text{rad.}]_s$ with log λ is found experimentally.

Now $\log \lambda - \log m = \log \tau_s$ (III)

Therefore the displacement between the two curves is a measure of τ_s.

To measure relative radical concentration a "pilot" reaction, whose rate is first power with respect to radical concentration is necessary. In the aldehyde system, the hydrogen abstraction reaction to give propane is unsuitable, because propane is also produced by the primary photolytic act. This defect does not apply to the ketone source of isopropyl. However the high disproportionation rate means that propane from abstraction is much less than that from disproportionation, if second-order termination predominates. Thus the experimental error in measuring the abstraction rate is large. Some preliminary work with di-isopropyl ketone yielded very scattered results. The problem was solved by photolysing the aldehyde in the

presence of ethylene. The rate of addition of isopropyl to the double bond was followed by measuring the rate of isopentane formation. Corrections to this measurement are discussed later.

In the low temperature photolysis of isobutyraldehyde there are two reactions which destroy radicals, the combination of isopropyl to give 2:3 dimethyl butane,

$$2\ C_3H_7 \xrightarrow{k_1} C_6H_{14} \qquad (1)$$

and the disproportionation

$$2\ C_3H_7 \xrightarrow{k_2} C_3H_8 + C_3H_6 \qquad (2)$$

From reaction (1) $R_{C_6H_{14}} = k_1[C_3H_7]^2$ (IV)

Now $[C_3H_7]_s = \tau_s\ R_{C_3H_7\ s}$ (V)

Under steady conditions the rates of production and destruction of the radical are equal.

$$\therefore R_{C_3H_7\ s} = 2(R_{C_6H_{14}\ s} + R_{C_3H_6\ s})$$

$$= 2 \times 1.65\ R_{C_6H_{14}\ s} \qquad (VI)$$

since $k_2/k_1 = 0.65$[31]

Hence $k_1 = 1/(4\tau_s^2\ 1.65^2\ R_{C_6H_{14}\ s})$ (VII)

Corrections made to the theoretical curve to allow for first-order termination are discussed later.

4.2 EXPERIMENTAL

Isobutyraldehyde, B.D.H., and Analar acetone, B.D.H., were shown to be pure by gas chromatography, and by the nature of their photolytic

products. Ethylene, B.O.C., contained less than 1% propylene.

The illumination and temperature control have already been described in Section 2.5.

The analysis of the condensable fraction of the products was made on a column (300 cm. x 0.5 cm.) packed with 5% squalane/40-60 mesh activated alumina, which was heated during the analysis and rose from 20° to 120° in 30 minutes.

4.3 RESULTS AND DISCUSSION

The reaction scheme has already been investigated[31] and the principal reactions below 170°C are as in the scheme below.

$$(CH_3)_2CH.CHO + h\nu \longrightarrow \begin{cases} C_3H_7 + CHO & (a) \\ C_3H_8 + CO & (b) \\ CH_3 + C_2H_4CHO & (c) \end{cases}$$

$$2\ C_3H_7 \xrightarrow{k_1} C_6H_{14} \quad (1)$$

$$2\ C_3H_7 \xrightarrow{k_2} C_3H_8 + C_3H_6 \quad (2)$$

$$C_3H_7 + C_3H_7CHO \xrightarrow{k_3} C_3H_8 + C_3H_7CO \quad (3)$$

$$C_3H_7CO \longrightarrow C_3H_7 + CO \quad (3a)$$

$$C_3H_7 + C_2H_4 \xrightarrow{k_4} C_5H_{11} \quad (4)$$

$$C_5H_{11} + C_3H_7CHO \xrightarrow{k_5} C_5H_{12} + C_3H_7CO \quad (5)$$

$$C_5H_{11} + C_2H_4 \xrightarrow{k_6} C_7H_{15} \quad (6)$$

$$C_3H_7 + C_5H_{11} \xrightarrow{k_7} C_8H_{18} \quad (7)$$

$$C_3H_7 + C_5H_{11} \xrightarrow{k_8} C_5H_{12} + C_3H_6 \quad (8)$$

$$C_3H_7 + C_5H_{11} \xrightarrow{k_9} C_3H_8 + C_5H_{10} \quad (9)$$

$$2\ C_5H_{11} \xrightarrow{k_{10}} C_{10}H_{22} \quad (10)$$

$$2\ C_5H_{11} \xrightarrow{k_{11}} C_5H_{12} + C_5H_{10} \quad (11)$$

The photolytic process (c) is unimportant, the methane produced is negligible. Reaction (4) was used as a measure of isopropyl concentration. Reactions (5) to (11) show the ways in which isopentyl may further react. Reaction (5) predominates, and in practice the rate of isopentane formation was used to measure isopropyl concentration.

$$R_{C_5H_{12}} = k_4[C_3H_7][C_2H_4] \qquad \text{from (4), (5)}$$

$$\text{Hence} \qquad \frac{[C_3H_7]_i}{[C_3H_7]_s} = \frac{R_{C_5H_{12}\ i}\ [C_2H_4]_s}{R_{C_5H_{12}\ s}\ [C_2H_4]_i}$$

Reaction (5) regenerates isopropyl, so the addition is not a termination reaction.

Runs with alternate steady and intermittent illumination were made, and each intermittent run compared with at least two steady runs, usually those preceding and following, to obtain mean $[C_3H_7]_i/[C_3H_7]_s$. The steady runs used for comparison are shown in Tables 4.1 - 4.3. Intermittent runs were three times the length of steady runs. Aldehyde consumption did not exceed 10%, nor ethylene consumption 2%. Although the temperature was held constant to within $\pm$ 0.7°C, small corrections were made to the rate of isopentane formation, it was normalised to the required temperature using the data of Kerr and Trotman-Dickenson[31] on the addition of isopropyl to ethylene.

The experimental values of $[C_3H_7]_i/[C_3H_7]_s$ were plotted against $\log \lambda + \frac{1}{2} \log R_{C_6H_{14}\ s}$ to correct for small light intensity fluctuations.

From (VII), $\log k_1 = 12 - \log(4 \times 1.65^2) - 2 \log \tau_s - \log R_{C_6H_{14}\ s}$.

Since $R_{C_6H_{14}}$ has the units 10^{-12} moles. cm.$^{-3}$ sec.$^{-1}$

$$\log k_1 = 10.96 - (2 \log \tau_s + \log R_{C_6H_{14}\ s})$$

If $d = (\log \lambda + \frac{1}{2} \log R_{C_6H_{14}\ s}) - \log m = \log \tau_s - \frac{1}{2} \log R_{C_6H_{14}\ s}$

Then $\log k_1 = 10.96 - 2d$.

At aldehyde concentrations of $1.2 - 1.4.10^{-6}$ moles. cm.$^{-3}$ and suitable ethylene concentrations, determinations of k_1 were made at 81°C, 115°C and 169°C. Tables 4.1, 4.2 and 4.3 record the conditions, products and values of $[C_3H_7]_i/[C_3H_7]_s$ derived from the runs. There were changes in light intensity after runs 25, 30 and 54 owing to changing the lamp and cleaning the cell. Figures 4.1 - 4.3 show the experimental plots and the best fit with the theoretical curves. The filled circles in Figure 4.1 represent low ethylene concentration. The values for $\log k_1$ from the plots are given in Table 4.4 as the uncorrected rate constant. Thus within experimental error there is no temperature coefficient and

$$k_1 = 10^{14.5} \text{ moles.}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}$$

Corrections. If the only reactions removing isopropyl are (1) and (2), then the radical concentration depends on the square root of the light intensity, and this may be monitored by $R^{\frac{1}{2}}_{C_6H_{14}}$. Thus it should be possible to correct for any run to run intensity fluctuations, by multiplying $[C_3H_7]_i/[C_3H_7]_s$ by the factor $R^{\frac{1}{2}}_{C_6H_{14}\ s}/2\ R^{\frac{1}{2}}_{C_6H_{14}\ i}$. Ideally this ratio should be 1.0, in fact

the average value was 1.08.

The well-established acetone system was used to check the experimental technique. The corresponding ethane ratio was exactly one. Thus experimental effects, such as a light intensity loss owing to cooling of the lamp by the sector, are precluded. The photolysis of the aldehyde alone also gave a ratio very close to one, and a few runs made at 81°C with half the usual ethylene concentration, gave a ratio 1.04. Thus this effect must be due to a reaction involving ethylene or isopentyl.

In the above scheme reaction (3) and reaction (4) followed by (5) and (6) will regenerate isopropyl, and so do not affect its concentration. However if (4) is followed by any of reactions (7) to (11), it constitutes a chain-terminating process which is first-order with respect to isopropyl concentration. The concentration of isopentyl is small compared with isopropyl, therefore reactions (10) and (11) will be ignored. The predominating reaction between isopropyl and isopentyl will be (7), the cross-combination. Octane was not definitely identified, but the presence of a small amount, appearing as a wide peak at the same time as the aldehyde began to be eluted, cannot be excluded. Such a small amount could not have been accurately measured under these conditions, although an upper limit may be set on it. The following estimation of the first-order termination was made.

From (3) $$k_3/k_1^{\frac{1}{2}} = \frac{R_{C_3H_8}\ (3)}{[\text{Ald.}]\ R^{\frac{1}{2}}_{C_6H_{14}}},$$

from (5) $$k_5/k_{10}^{\frac{1}{2}} = \frac{R_{C_5H_{12}}}{[\text{Ald.}]\ R^{\frac{1}{2}}_{C_{10}H_{22}}},$$

$k_3/k_1^{\frac{1}{2}}$ has been determined,[31] $k_5/k_{10}^{\frac{1}{2}}$ has not, but it is known that the analagous rate constant ratio is similar for ethyl,[33] propyl[30,31] and butyl,[29,32,34,35] so will probably be about the same for isopentyl. For calculation purposes it is assumed that isopentyl behaves like isobutyl. The ratio $(k_5/k_{10}^{\frac{1}{2}})/(k_3/k_1^{\frac{1}{2}})$ was calculated at each temperature on this basis, as was about 1.8.

$$\text{Thus} \qquad \frac{R_{C_5H_{10}}}{R^{\frac{1}{2}}_{C_{10}H_{22}}} = \frac{1.8\ R_{C_3H_8}\ (3)}{R^{\frac{1}{2}}_{C_6H_{14}}}$$

$$\text{Now} \qquad R_{C_8H_{18}} = 2\ R^{\frac{1}{2}}_{C_6H_{14}}\ R^{\frac{1}{2}}_{C_{10}H_{22}}$$

$$\therefore \qquad R_{C_8H_{18}} = \frac{2\ R_{C_6H_{14}}\ R_{C_5H_{12}}}{1.8\ R_{C_3H_8}\ (3)}$$

where $R_{C_3H_8}\ (3) = R_{C_3H_8}\ (\text{total}) - R_{C_3H_6} - R_{C_3H_8}\ (b)$

Reasonable estimates may be made for propane from the photolytic act. Propylene production was calculated as $0.65\ R_{C_6H_{14}}$ because the ethylene contained a small propylene impurity.

At each temperature mean values of the rate of octane formation, under steady and intermittent illumination were estimated. By analogy with isobutyl we may estimate $(k_8 + k_9)/k_7 = 0.3$. This estimation is uncertain, but has little effect on the calculation.

Hence First-order termination $= 2 \times 1.3 \times R_{C_8H_{18}}$

since each of reactions (7) to (9) effectively destroy two isopropyls.

$$\therefore \quad \alpha_c = \frac{\text{First order termination}}{\text{Second order termination}} = \frac{1.3 \times R_{C_8H_{18}}}{1.65 \times R_{C_6H_{14}}}$$

This value was used to derive a new theoretical curve at each temperature using Shepp's[39] modified theory, which includes a first-order termination. If the total termination rate is substituted for that of hexane, in the expression $R^{\frac{1}{2}}_{C_6H_{14}\ s} / 2\ R^{\frac{1}{2}}_{C_6H_{14}\ i}$, then the discrepancy between theoretical and experimental values is more than halved. The remaining small discrepancy is within experimental error.

The rate of reaction (4) was followed by measuring isopentane formation, this estimates isopentyl disappearing by reactions (5), (8) and (11). Reaction (10) may be ignored. Reaction (6) will produce isoheptane, this was not detected but will be proportional to isopentane and so cancels. However isopentyls disappearing by (7) and (9) should be included.

Strictly, $$\frac{[C_3H_7]_i}{[C_3H_7]_s} = \frac{(R_{C_5H_{12}} + R_{C_7H_{16}} + R_{C_8H_{18}} + R_{C_5H_{10}})_i}{(R_{C_5H_{12}} + R_{C_7H_{16}} + R_{C_8H_{18}} + R_{C_5H_{10}})_s}$$

which closely approximates to

$$\frac{(R_{C_5H_{12}} + R_{C_8H_{18}})_i}{(R_{C_5H_{12}} + R_{C_8H_{18}})_s}$$

At each temperature a ratio was calculated from mean rates of octane and isopentane formation, which corresponded to a value of 0.375 using isopentane formation only. Thus the comparison was made on the most sensitive part of the curve. The fit between the two curves was altered, and a correction applied to the rate constant.

A final correction concerns the equating of the rate of radical production with termination.

$R_{termination} = (1 + \alpha_c)$ Second-order termination.

Therefore the expression for k_1 (VII) should be divided by $(1 + \alpha_c)^2$.

The rate constants and the corrections applied are summarised in Table 4.4.

TABLE 4.4 ISOPROPYL COMBINATION

Temperature °C	80.8	114.8	169.3
Uncorrected log k_1	14.52	14.50	14.42
α_c	0.23	0.20	0.21
First-order termination correction	- 0.72	- 0.64	- 0.66
Correction to $[C_3H_7]_i/[C_3H_7]_s$	+ 0.26	+ 0.18	+ 0.14
Correction to $R_{C_3H_7\ s}$	- 0.18	- 0.16	- 0.16
Corrected log k_1	13.88	13.88	13.74

The corrected rate constants yield a negative activation energy of 1.3 k. cal. mole.$^{-1}$. However this depends only on the determination at 169°C, where the points are more scattered than at lower temperatures. It is approximately equal to the 95% confidence error, so little importance is attached to it. If the activation energy is zero, then

$$\log A_1 = 13.8 \left(\text{mole.}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}\right)$$

The corrections applied introduce uncertainty into the rate constants. However the estimation of octane is unlikely to be far

in error. The assumption that isopentyl resembles isobutyl, and therefore $(k_5/k_{10}^{\frac{1}{2}})/(k_3/k_1^{\frac{1}{2}})$ is 1.8, probably underestimates octane. However had the amount of octane been much larger it could have been definitely measured. Also, if α_c were much greater than 0.2 the upper limiting value of $[C_3H_7]_i/[C_3H_7]_s$ would be lower than the limiting values found experimentally. This experimental upper limit also shows that no other first-order termination, such as

$$C_3H_7 + CHO \longrightarrow C_3H_7CHO \qquad (12)$$

takes place to a significant extent.

The few determinations made at 81°C with low ethylene concentration do not fit the simple curve well, nor the corrected curve with $\alpha_c = 0.23$. However they would better correspond to a curve for which α_c is about 0.1, a reasonable value at low ethylene concentration.

It is also observed that if the anomalous value of $R^{\frac{1}{2}}_{C_6H_{14}\ s}/R^{\frac{1}{2}}_{C_6H_{14}\ i}$ were attributed to a real variation in light intensity, and the experimental values were corrected accordingly, then within experimental error, the temperature coefficient is zero, and

$$\log A_1 = 13.9 \left(\text{mole.}^{-1}\ \text{cm.}^3\ \text{sec.}^{-1}\right)$$

Thus the uncertainty lies only in the A factor, the activation energy is zero no matter what correction is applied.

If a collision diameter of 4.75 Å is assumed for isopropyl, equating it with that calculated by Rowlinson[158] for propane, and the activation energy is zero, the collision rate at 115°C is $10^{14.12}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$. The experimental rate of bimolecular

termination at 115°C, including combination and disproportionation, is $10^{14.16}$ mole.$^{-1}$ cm.^{3} sec.$^{-1}$, giving the reaction a steric factor of about unity.

The relation between this combination and the reverse reaction, the symmetrical decomposition of 2:3 dimethyl butane is considered in Section 6.3.

Notes on Tables 4.1 - 4.3

Rates of formation of products are given in 10^{-12} moles. cm.$^{-3}$ sec.$^{-1}$.

$[C_2H_4]$ is mean ethylene concentration in 10^{-6} moles. cm.$^{-3}$.

a.f. = analytical failure.

i, s = intermittent, steady, illuminations.

λ = length light flash in secs.

C_5H_{12} - isopentane.

C_6H_{14} - 2:3,-dimethyl butane.

TABLE 4.1 $81^{\circ}C$

Run	Mean $[C_2H_4]$	$R_{C_3H_8}$	$R_{C_3H_6}$	R_{CO}	$R_{C_5H_{12}}$	$R_{C_6H_{14}}$	Mean $\frac{[C_3H_7]_i}{[C_3H_7]_s}$	Comparative steady runs	$\log\lambda + \frac{1}{2}\log R_{C_6H_{14}}$ s
80	4.17	47.0	14.5	74.2	6.97	10.1	-	-	-
81	3.91	12.3	2.48	19.3	2.42	1.95	0.377	80, 82	$\bar{2}.750$
82	4.07	47.0	8.80	73.5	6.60	10.7	-	-	-
83	3.75	12.6	2.18	19.9	2.78	2.11	0.451	82, 84	$\bar{2}.125$
84	4.17	49.0	10.5	73.6	6.94	10.1	-	-	-
85	3.91	12.4	2.81	18.9	2.30	1.98	0.337	84, 86	$\bar{1}.419$
86	3.88	48.1	10.8	74.1	7.15	10.1	-	-	-
87	4.01	12.0	a.f.	19.8	2.54	2.20	0.346	86, 88	$\bar{1}.092$
88	3.84	50.0	11.4	75.6	6.97	9.40	-	-	-
89	3.88	12.0	2.74	19.3	2.58	2.24	0.362	88, 90	$\bar{2}.882$
90	3.96	50.3	9.08	73.3	7.36	10.5	-	-	-
91	3.94	a.f.	a.f.	20.4	3.12	2.37	0.430	90, 92	$\bar{2}.448$
92	3.96	52.0	9.23	75.7	7.25	10.1	-	-	-
93	3.80	12.6	3.05	19.9	3.09	2.45	0.446	92, 96	$\bar{2}.395$
94	3.97	12.7	2.47	19.5	3.29	2.23	0.454	92, 96	$\bar{2}.134$
96	4.32	48.3	8.53	75.7	7.87	10.5	-	-	-
97	3.88	12.6	2.74	17.7	2.25	2.48	0.309	96, 98	$\bar{1}.550$
98	3.99	50.7	9.29	75.0	7.77	10.0	-	-	-
106	1.75	55.4	9.78	71.6	3.75	11.1	-	-	-
107	1.76	13.5	2.28	18.5	1.64	2.46	0.440	106, 108	$\bar{2}.362$
108	1.79	47.3	6.40	67.9	3.80	10.7	-	-	-
109	1.77	11.9	1.76	19.4	1.60	2.48	0.439	108, 110	$\bar{2}.622$
110	1.80	48.5	8.22	71.2	3.62	10.4	-	-	-
111	1.81	11.2	1.64	17.2	1.48	2.19	0.428	110, 112	$\bar{2}.720$
112	1.79	47.5	9.60	67.6	3.27	9.25	-	-	-

FIGURE 4·1 81°C

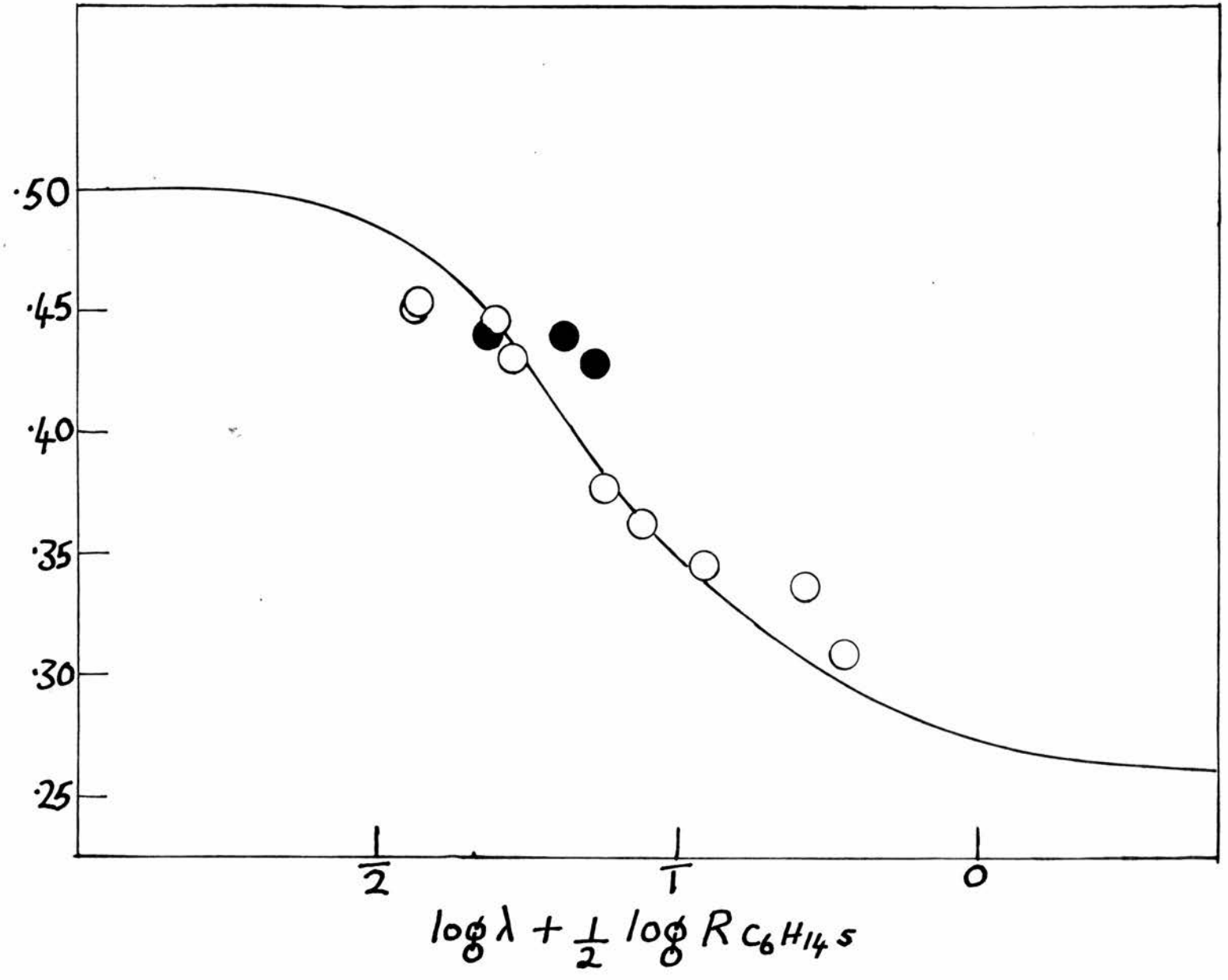


TABLE 4.2 115°C

Run	$[C_2H_4]$	$R_{C_3H_8}$	$R_{C_3H_6}$	R_{CO}	$R_{C_5H_{12}}$	$R_{C_6H_{14}}$	Mean $\frac{[C_3H_7]_i}{[C_3H_7]_s}$	Comparative steady runs	$\log\lambda + \frac{1}{3}\log R_{C_6H_{14}s}$
15	2.00	68.1	11.8	112	10.4	12.7	-	-	-
17	2.19	75.9	14.4	118	11.5	11.9	-	-	-
18	2.10	21.2	6.9	33.5	5.25	3.12	0.471	15, 17, 20	$\bar{2}.219$
19	2.10	18.6	2.9	33.8	5.17	2.04	0.462	15, 17, 20	$\bar{2}.221$
20	2.10	73.6	12.3	113	11.6	12.1	-	-	-
21	2.13	20.3	2.5	30.7	3.32	2.42	0.294	15, 17, 20	$\bar{1}.435$
22	2.10	74.6	15.5	108	10.9	12.5	-	-	-
23	2.24	18.4	4.1	32.1	4.08	2.08	0.355	20, 22, 24	$\bar{1}.019$
24	2.03	72.5	11.0	117	9.57	a.f.	-	-	-
25	2.15	16.7	4.2	28.1	4.21	2.21	0.383	20, 22, 24	$\bar{2}.794$
27	2.14	80.8	12.3	130	11.0	10.9	-	-	-
28	2.08	15.9	4.51	31.0	4.74	2.13	0.446	27, 29	$\bar{2}.336$
29	2.10	54.8	11.9	110	10.6	8.60	-	-	-
30	2.12	15.2	2.32	29.5	3.46	1.91	0.319	27, 29	$\bar{1}.077$
33	2.01	53.2	11.8	100	8.66	8.70	-	-	-
34	2.03	13.8	2.60	27.7	3.49	1.48	0.424	33, 35, 37	$\bar{2}.485$
35	2.13	52.0	8.25	99.8	8.07	8.01	-	-	-
36	2.06	12.5	1.93	24.6	1.94	1.80	0.232	33, 35, 37	1.450
37	2.11	53.9	8.58	99.9	8.66	8.23	-	-	-

FIGURE 4·2 115°C

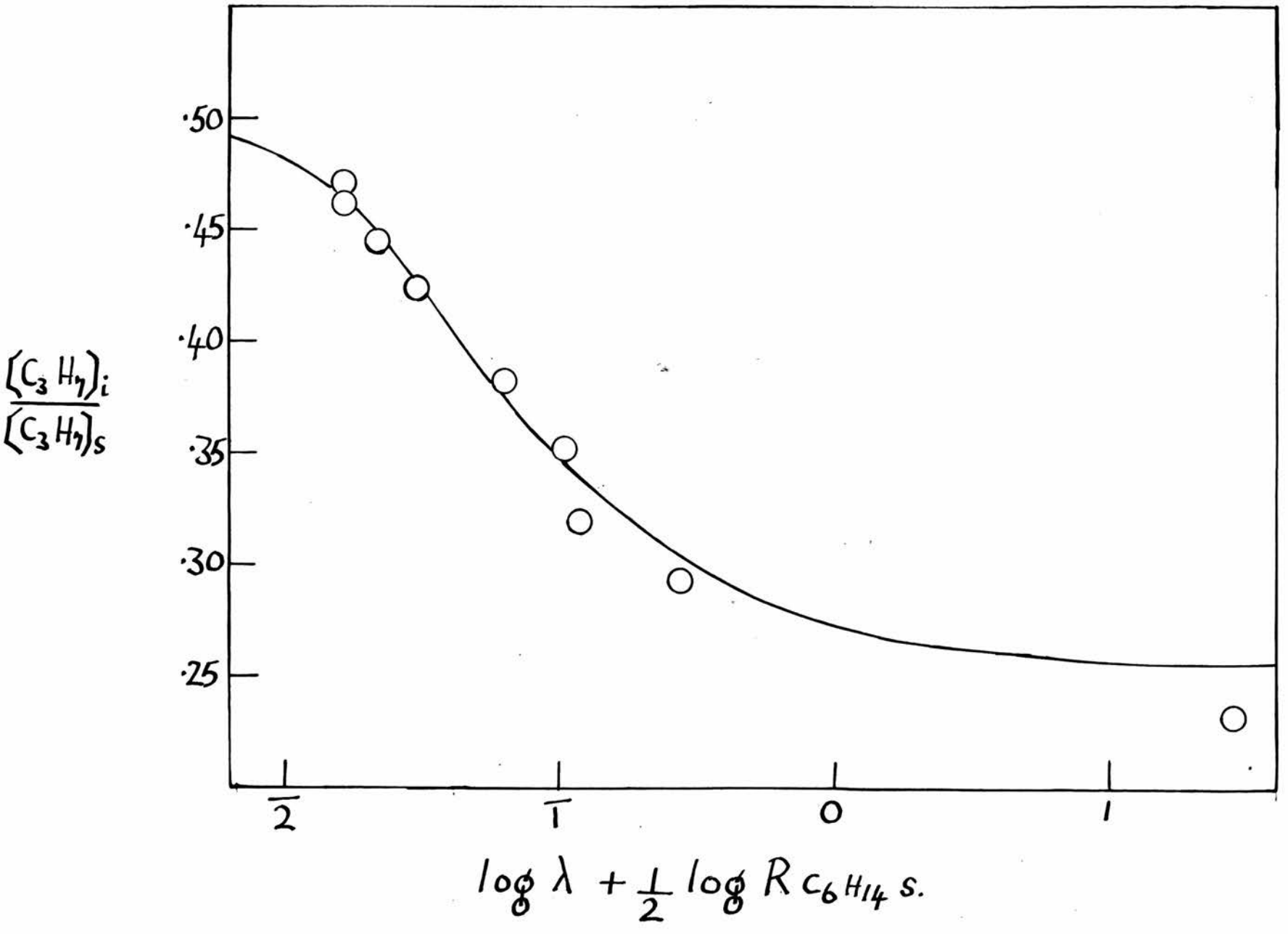
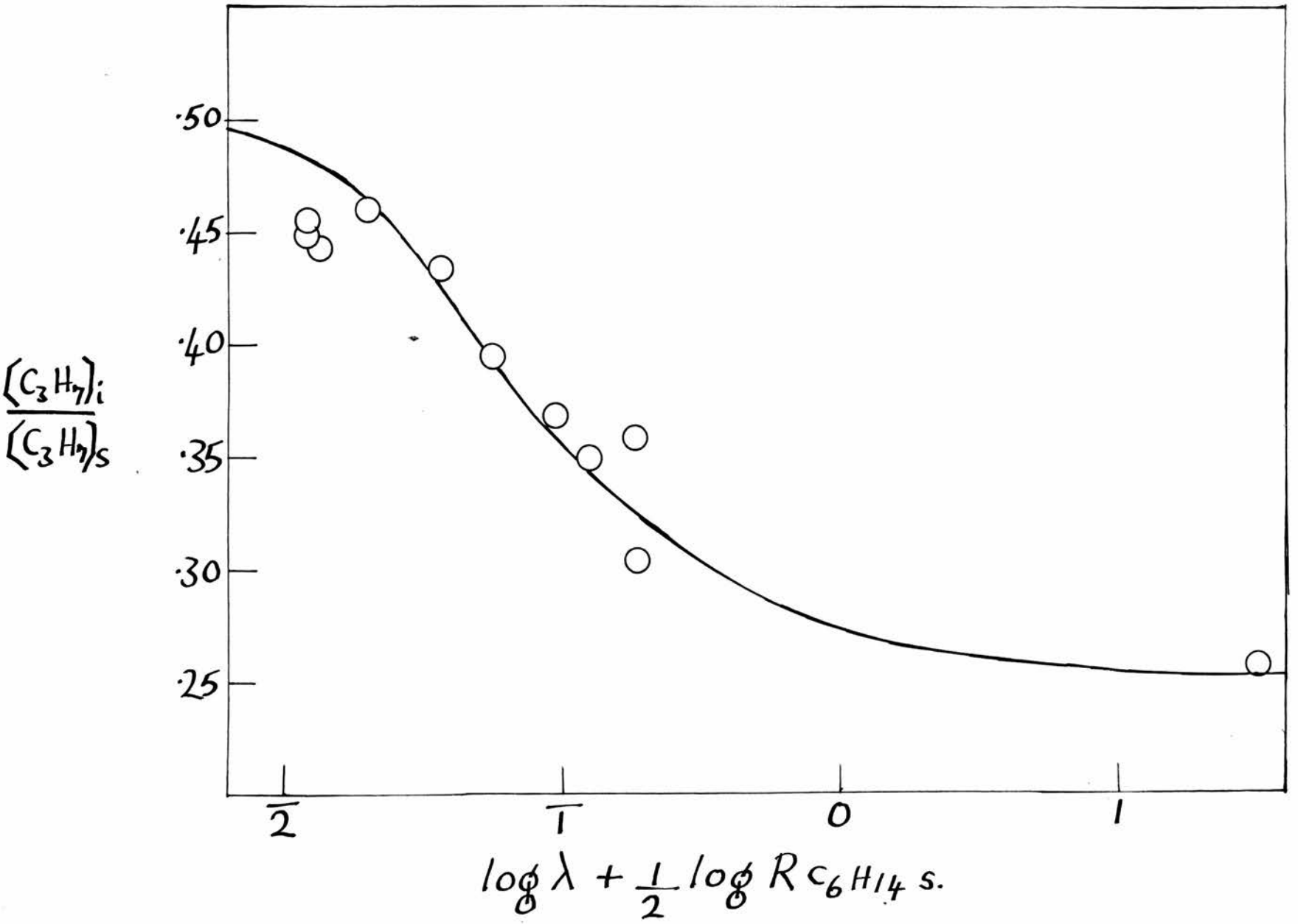


TABLE 4.3 169°C

Run	$[C_2H_4]$	$R_{C_3H_8}$	$R_{C_3H_6}$	R_{CO}	$R_{C_5H_{12}}$	$R_{C_6H_{14}}$	Mean $\frac{[C_3H_7]_i}{[C_3H_7]_s}$	Comparative steady runs	$\log \lambda + \frac{1}{2} \log R_{C_6H_{14}\,s}$
40	2.19	80.5	10.6	145	31.5	8.95	-	-	-
41	1.09	83.2	8.85	133	17.4	9.66	-	-	-
42	1.10	23.0	2.06	40.2	7.63	1.78	0.442	40, 41, 43	$\bar{2}.127$
43	1.10	92.2	9.66	136	18.6	7.74	-	-	-
44	1.17	21.1	1.91	35.6	5.95	1.90	0.305	43, 45	$\bar{1}.269$
45	1.13	85.3	1.06	135	18.8	8.92	-	-	-
46	1.11	22.5	2.23	38.7	6.98	1.84	0.369	45, 47	$\bar{2}.985$
47	1.11	95.9	8.98	131	18.9	8.55	-	-	-
48	1.11	21.5	1.79	37.9	7.30	1.71	0.396	47, 49	$\bar{2}.757$
49	1.20	81.0	9.49	132	19.1	7.63	-	-	-
50	1.14	25.5	2.19	39.4	7.99	1.75	0.434	49, 52	$\bar{2}.569$
51	1.09	23.2	2.11	39.7	8.01	1.51	0.456	49, 52	$\bar{2}.087$
52	1.19	88.2	9.97	130	19.5	8.62	-	-	-
53	1.13	21.0	3.96	36.3	6.43	1.66	0.350	52, 54	$\bar{1}.091$
54	1.11	86.7	9.39	132	18.1	8.11	-	-	-
56	1.08	93.2	10.7	143	17.9	9.67	-	-	-
57	1.09	26.0	2.10	42.0	8.77	1.78	0.459	56, 58	$\bar{2}.319$
58	1.08	90.1	11.2	144	20.5	9.11	-	-	-
59	1.13	27.7	2.58	41.3	7.15	2.29	0.357	58, 60	$\bar{1}.251$
60	1.08	89.8	10.6	139	17.3	8.70	-	-	-
61	1.19	27.1	2.36	42.6	9.22	2.04	0.499	60, 62	$\bar{2}.093$
62	1.15	102	10.0	143	21.5	10.1	-	-	-
63	1.11	22.0	2.58	37.1	4.90	2.49	0.257	60, 62	1.502

FIGURE 4·3 169°C



CHAPTER V

INHIBITION BY NITRIC OXIDE AND OXYGEN IN KETONE PHOTOLYSES

Summary. The photolyses of diethyl ketone with added nitric oxide, and methyl n-propyl ketone with added nitric oxide and oxygen, were used as a test of the effectiveness of these inhibitors in ketone photolyses. The photolytic acts have already been investigated[7,158,159] and are well understood. The investigation was made in the hope that the use of nitric oxide could be extended to investigate the primary photolytic acts of aldehydes.

5.1 EXPERIMENTAL

Diethyl ketone, B.D.H., and methyl n-propyl ketone, B.D.H., were shown to be pure by gas chromatography, and by the nature of their photolytic products. Nitric oxide was prepared by dropping conc. hydrochloric acid on sodium nitrite and potassium iodide. It was purified by distillation from -183°C to -200°C. Oxygen from a B.O.C. commercial cylinder was free from condensables, but was not nitrogen free.

The analysis of the condensable fraction of the products was made on a column (150 x 0.5 cm.) packed with 1% squalane/60-90 mesh activated alumina, which was heated during the analysis, and the temperature rose from 20°C to 100°C in 60 minutes. Some later runs were analysed on a column (140 x 0.5 cm.) packed with 60-90 mesh activated alumina, which was heated to 120°C during the first 20

minutes of the analysis.

The general apparatus and illumination, the unfiltered light from a medium-pressure mercury arc, were the same as those described in Section 2.1. In runs in which large amounts of nitric oxide were added, an analysis of the non-condensables was made, but the methane and carbon monoxide fractions were probably contaminated with nitric oxide, and are therefore unreliable. No attempt was made to analyse for non-condensables in runs in which oxygen was added.

5.2 RESULTS AND DISCUSSION

The conditions, products and the rates of their formation, derived from the runs are summarised in Tables 5.2A and 5.2B.

Diethyl ketone. Photolyses were made at 145°C and 210°C. Ketone pressure varied between 30 and 40 mm. The pressure of added nitric oxide was varied between zero and 105 mm. When the nitric oxide pressure:ketone pressure exceeded 2:3, the products of radical combination, disproportionation and abstraction were completely suppressed.

However even at high inhibitor pressure a small, nearly constant, amount of ethylene was produced. This could be formed by the reaction

$$C_2H_5 + NO \longrightarrow C_2H_4 + HNO$$

The rate of ethylene formation increased slightly with increasing nitric oxide concentration. Alternatively it could result from a primary process:

$$C_2H_5COC_2H_5 + h\nu \longrightarrow C_2H_4 + C_2H_5CHO$$

If $\phi_{CO} = 1.0$,[158] then $\phi_{C_2H_4} = 0.03$.

Methyl n-propyl ketone. Photolyses were made at 145°C, 30 mm. ketone pressure, alone and with added nitric oxide. Photolyses were also carried out at 85°C and 168°C with added oxygen. Minimum pressures of 20 mm. of either inhibitor were used, and were sufficient to suppress all radical reactions.

At high pressure of either inhibitor, ethylene was still produced at the same rate as in the uninhibited photolysis. This is formed by the well-known intramolecular process[7,159] producing an olefin and a lower ketone. The ethylene yield was independent of temperature. Borkowski and Ausloos[159] found that $\phi_{C_2H_4}$ decreased with increasing oxygen pressure in the photolysis of methyl 2:3:3-trideutero n-propyl ketone. The present work does not show this effect, but Borkowski and Ausloos found the effect less marked at short wavelengths, and with the undeuterated ketone.

A small amount of propylene was still produced at high nitric oxide pressure. It was not positively identified in runs with added oxygen, because of the presence of relatively large amounts of an oxygenated compound eluted at the same time. The propylene may be formed by the reaction of n-propyl with nitric oxide:

$$C_3H_7 + NO \longrightarrow C_3H_6 + HNO$$

or by a primary process:

$$C_3H_7COCH_3 + h\nu \longrightarrow C_3H_6 + CH_3CHO$$

Comparing with the photolysis of diethyl ketone in which $\phi_{CO} = 1.0$,[158] the quantum yields are $\phi_{CO} = 0.14$, $\phi_{C_2H_4} = 0.15$ and $\phi_{C_3H_6} = 0.01$. Borkowski and Ausloos also found the quantum yields

of carbon monoxide and ethylene equal at short wave-lengths in the photolysis of methyl 2:3:3 trideutero n-propyl ketone, although their value was 0.42.

Both nitric oxide and oxygen are efficient inhibitors of radical processes in these ketone photolyses, when added at sufficient pressure.

TABLE 5.2A DIETHYL KETONE AND NITRIC OXIDE

Run	Temperature °C	[ketone] Initial	Pressure NO mm.	R_{H_2}	R_{CH_4}	R_{CO}	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_4H_{10}}$
7	146	1.27	-	14.0	1.5	335	180	24.2	145
5	144	1.49	9.0	6.1	26.0	296	44.0	33.3	75.8
11	144	1.26	11.7	3.5	35.0	140	2.9	a.f.	14.3
13	146	1.26	12.8	6.2	14.0	155	18.3	21.9	5.7
10	147	1.27	24.1	2.0	60.0	66.2	0.4	a.f.	0.0
12	146	1.29	35.0	1.3	59.0	31.0	0.0	8.7	0.0
16	209	1.09	37.0	2.0	29.0	165	0.0	6.1	0.0
14	144	1.31	43.7	3.9	44.0	40.4	0.0	9.5	0.0
17	211	1.25	45.6	6.5	30.2	266	0.0	11.3	0.0
15	146	1.27	60.1	1.4	60.3	41.4	0.0	9.5	0.0
18	209	1.25	105	1.7	134	161	0.0	12.1	0.0

a.f. = analytical failure

ketone concentration in 10^{-6} moles. cm.$^{-3}$

R_{H_2} etc. in 10^{-12} moles. cm.$^{-3}$ sec.$^{-1}$

TABLE 5.2B METHYL n PROPYL KETONE AND NITRIC OXIDE/OXYGEN

Run	Temperature °C	[ketone] Initial	Pressure mm.	NO	R_{H_2}	R_{CH_4}	R_{CO}	$R_{C_2H_6}$	$R_{C_2H_4}$	$R_{C_3H_8}$	$R_{C_3H_6}$	$R_{C_4H_{10}}$
24	144	1.30	-	0.60	16.3	49.9	10.4	41.8	4.6	2.7	12.6	
27	140	1.26	-	1.04	12.6	41.4	7.9	40.9	5.4	2.7	10.5	
29	143	0.924	35.1	1.09	12.5	8.2	0.0	30.5	0.0	2.2	0.0	
21	149	1.25	41.1	a.f.	24.6	14.9	0.0	34.9	0.0	a.f.	0.0	
22	150	1.25	43.8	0.69	21.6	14.9	0.0	52.9	0.0	1.4	0.0	
25	143	1.25	44.9	1.47	19.3	11.8	0.0	37.5	0.0	1.4	0.0	
26	148	1.24	46.9	0.53	20.5	11.5	0.0	45.9	0.0	1.9	0.0	
20	144	1.28	63.7	0.64	48.5	4.4	0.0	76.6	0.0	4.6	0.0	
			Pressure mm.	O_2								
33	168	1.22	20.5				0.0	42.7	0.0	a.f.	0.0	
32	86	1.29	29.7				0.0	40.9	0.0	a.f.	0.0	
34	165	1.20	35.4	not measured			0.0	52.0	0.0	a.f.	0.0	
30	87	1.43	38.9				0.0	41.8	0.0	a.f.	0.0	
31	86	1.18	77.3				0.0	40.9	0.0	a.f.	0.0	

CHAPTER VI

DISCUSSION OF ABSOLUTE COMBINATION RATES OF ALKYL RADICALS

6.1 SYSTEMS USED FOR INTERMITTENT ILLUMINATION STUDIES

Before a study may be made using intermittent illumination the mechanism of the photolysis must be well-understood. Most studies have concerned the photolysis of ketones. Relative radical concentration is measured by the rate of hydrogen abstraction from the parent ketone to give an alkane. This reaction results in a first-order termination and conditions must be adjusted so that second-order termination predominates. The fraction of first-order termination can be estimated and corrections made.

This method is ideal when combination is the only second-order termination reaction, as is the case for methyl and trifluoromethyl radicals. If disproportionation also occurs, but the ratio of disproportionation to combination (k_d/k_c) is low, e.g. 0.14 for ethyl, 0.16 for n-propyl, this method may still be used. However if the disproportionation ratio is relatively high, say above 0.30, the alkane from abstraction will be less than that from disproportionation, when second-order termination predominates. For isopropyl, for which $k_d/k_c = 0.65$,[31] the propane produced by abstraction from the ketone will be 20% or less of that from disproportionation, under suitable conditions. This seriously limits the accuracy of the results. Preliminary work carried out on the photolysis of di-isopropyl ketone was abandoned, because results were too scattered.

Even in the case of di-n-propyl ketone, from which an anomalously high rate constant for n-propyl combination was obtained, the authors[57] suggest that this difficulty may have contributed to the high result. Thus although ketone photolyses are well understood and have been used with success, they are unsuitable for the study of combination rates of higher alkyl radicals. A possible exception is di-isobutyl ketone, the ratio k_d/k_c is 0.17[35] for isobutyl.

The photolysis of an alkyl mercury compound under intermittent illumination has only been investigated once, that of diethyl mercury by Ivin and Steacie.[55] The value obtained for the termination rate constant was reasonable, but in general the mechanisms of these photolyses are not well understood.

Aldehyde photolyses under intermittent illumination have been confined to acetaldehyde until recently. In the acetaldehyde work[43-5] there was doubt as to the nature of the termination process measured, a complete analysis of the products would probably have improved the understanding of the mechanism. An inherent advantage of the aldehyde photolysis is the regeneration of the radical, after hydrogen abstraction from the parent aldehyde. Thus abstraction is not a first-order termination and may be allowed to predominate over second-order termination. A disadvantage is the formation of the same alkane by hydrogen abstraction and by the primary photolytic act.

The present work on isopropyl combination was preceded by some exploratory work on the photolysis of isobutyraldehyde alone, using intermittent illumination. It was hoped to keep the fraction of propane formed in the primary act low by raising the temperature.

However a sufficiently high temperature meant the hexane could not be measured directly, which was undesirable.

An attempt to estimate the propane from the primary act by nitric oxide inhibition was also unsuccessful, the results did not show sufficient precision. The work in Chapter V showed that this inhibitor will effectively suppress radical reactions in ketone photolyses, but this does not prove that the same is true for aldehyde photolyses. The presence of formyl may be a complicating factor.

However aldehyde photolyses may be used if a suitable marker is added to determine relative radical concentrations. In the present work ethylene was used as a marker, the rate of radical addition to the double bond being first power with respect to radical concentration. The advantage of the aldehyde, of regenerating the original radical after hydrogen abstraction by any radical from the parent aldehyde, is retained. In the case of isopropyl, an isopentyl radical will be formed by addition, and after abstraction from the aldehyde, isopropyl is regenerated. Thus the marker reaction need not be limited to 10% of the second-order termination, which improves the precision of the results. The disadvantage is the possibility of other reactions of the isopentyl formed constituting a first-order termination, in particular cross-combination with isopropyl. Thus a first-order termination correction is necessary, as it was in the ketone photolyses.

A further disadvantage of using an aldehyde photolysis for this study, is the possibility of a termination reaction between an alkyl

radical and a formyl radical. At high temperatures alkyl radical concentration will be much higher than that of formyl, because of the chain regeneration of the alkyl, so such a reaction will be unimportant. The results of the isobutyraldehyde/ethylene photolysis also show that such a process cannot be important, because the shapes of the experimental curves set an upper limit to the amount of first-order termination occurring.

An intermittent illumination photolysis of alkyl azo compounds has not yet been attempted. The addition of the alkyl radical to the double bond of the azo compound would probably prove a serious complication.

6.2 COMPARISON OF ABSOLUTE COMBINATION RATES OF ALKYL RADICALS WITH THEORY

The rate constants, activation energies and A factors of alkyl radical combinations are summarised in Table 6.2A. For methyl only the most reliable value is given, that of Kistiakowsky and Roberts,[41] corrected by Shepp.[39] The maximum values of the activation energies for trifluoromethyl and ethyl combination were estimated by the authors from the experimental rate constants and maximum rates calculated from the collision theory.

The activation energies are all small, as was intuitively expected. The negative activation energy for isopropyl combination is within experimental error, so may be disregarded. Shepp and Kutschke[56] proposed that the 2 k. cal. mole.$^{-1}$ activation energy for ethyl combination is caused by the mutual repulsion of the C-H

bond orbitals as the radicals approach each other. They suggest that a similar activation energy will be found for higher alkyl radicals because the barrier will be the same for any CH_2 group. This effect was not found for isopropyl, but of course, as a secondary radical, it is unsuitable for comparison.

Making reasonable estimates for collision diameters,[156] calculations of collision rates at a particular temperature can be made. If the activation energy is assumed to be zero, the steric factor, P, can be calculated. Table 6.2B summarises the steric factors for alkyl radical combinations thus found.

The rate constant for n-propyl combination is much higher than the collision rate at this temperature, and is therefore unreliable, as the authors[57] pointed out. The other rate constants approach the collision rates at the same temperature. The steric factors are all greater than 0.1, and for isopropyl approach unity. It seems that alkyl radicals react on nearly every collision in the gas phase.

From the point of view of the collision theory high steric factors suggest that little orientation is required for alkyl radicals to combine. Viewed from the transition state theory angle, high A factors indicate high entropies of activation. These can only be explained by loosely-bound activated complexes, in which the radicals may rotate freely about the incipient C-C bond. Thus no rotational entropy is lost when the activated complex is formed.

Pressure effects. The combination of methyl radicals is pressure dependent below 5 mm. A third body is necessary to

deactivate the newly-formed energy-rich ethane molecules by collision, otherwise they will decompose again to yield two methyls. Marcus[52] correctly predicted the pressure range in which the methyl radical combination rate would fall off, on the assumption that the activated complex contained freely rotating methyl groups.

Brinton and Steacie[71] found that the ethyl combination rate was independent of pressure down to 0.01 mm. This is consistent with the larger number of degrees of freedom in the ethyl radical. Higher alkyl radical combinations are expected to be independent of pressure.

6.3 THE RELATION BETWEEN ALKYL RADICAL COMBINATIONS AND THE DECOMPOSITION OF ALKANES

Alkyl radical combinations are the reverse reactions of the symmetrical decomposition of alkanes. The Arrhenius parameters of the two reactions are related thermodynamically thus:

$$\Delta H = E_1 - E_{-1},$$

$$\Delta S = R \ln A_1/A_{-1},$$

where the subscripts, 1 and -1, refer to combination and decomposition respectively. Since E_1 is close to zero in all cases, the decomposition activation energy should equal the strength of the bond broken. For the decomposition of ethane this is 85 k. cal. mole.$^{-1}$ and Leigh, Szwarc and Eigeleisen[157] have determined the activation energy experimentally to be 85-9 k. cal. mole.$^{-1}$.

If the entropies of reactants and products are known the A factors of the forward and reverse reactions can be related.[153]

Entropies of radicals may be estimated as equal to the entropies of the alkanes with one more hydrogen atom, plus an additional term of R ln 2 i.e. 1.4 e.u., to allow for electron degeneracy. In this way the A factors of the symmetrical decomposition of ethane, n-butane and 2:3,dimethyl butane can be calculated. Because it is difficult to measure temperature coefficients, the A factors of combination are equated with the combination rate constants at 100°C. The results are summarised in Table 6.3.

TABLE 6.3

Alkane	$A_1 = \log k_1(100^\circ C)$ mole.$^{-1}$cm.^{3}sec.$^{-1}$	Ref.	ΔS e.u.	Calc. A_{-1} sec.$^{-1}$	Exp. A_{-1} sec.$^{-1}$	Ref.
Ethane	13.3	41, 39	-16.5	16.9	14.8-15.7	157
n Butane	13.3	56	-17.9	17.2	-	-
2:3 Dimethyl butane	13.9	Chapter IV	-23.9	19.1	-	-

Little reliance may be placed on the experimental determination of the A factor for ethane decomposition, because it is a preliminary value. However the calculated A factors for these decompositions are extremely high. They can only be explained if it is supposed that the incipient radicals rotate freely in three dimensions in the activated complex.[52] This is difficult to accept, but at present there is no alternative.

TABLE 6.2A ABSOLUTE COMBINATION RATES

Radical	log A mole.$^{-1}$ cm.^{3} sec.$^{-1}$	E k. cal. mole.$^{-1}$	log k (mole.$^{-1}$ cm.^{3} sec.$^{-1}$) Temp. in ^{o}C in parentheses	Reference
Methyl	13.34	0	13.34 (125-175)	41, 39
CD_3	-	-	13.58 (165)	41, 39
CF_3	-	≯1.5	13.36 (127)	54
Ethyl	-	≯0.65	13.20 (150)	55
	14.2	2 ± 1	13.18(50) 13.30(100) 13.62(150)	56
n Propyl	-	-	15.8 (100)	57
Isopropyl	13.8	-1 ± 1	13.88(81) 13.88(115) 13.74(169)	Chapter IV

TABLE 6.2B COMPARISON WITH COLLISION THEORY

Radical	log collision rate mole.$^{-1}$ cm.^{3} sec.$^{-1}$	Temp. ^{o}C	Collision diameter, Å	Experimental log k mole.$^{-1}$ cm.^{3} sec.$^{-1}$	P	Reference
Methyl	14.09	125	3.5	13.34	0.18	41, 39
CD_3	14.11	160	3.5	13.58	0.30	41, 39
CF_3	14.18	127	4.0	13.36	0.15	54
Ethyl	13.95 (a)	150	4.3	13.20	0.18	55
	14.03 (a)	50	4.3	13.18	0.14	56
	14.04 (a)	100	4.3	13.30	0.18	56
	14.05 (a)	150	4.3	13.62	0.37	56
n Propyl	14.07 (a)	100	4.75	15.8	-	57
Isopropyl	13.92 (a)	81	4.75	13.88	0.91	Chapter IV
	13.94 (a)	115	4.75	13.88	0.87	Chapter IV
	13.97 (a)	169	4.75	13.74	0.59	Chapter IV

Note:

(a) In calculating collision rates for ethyl and propyl, the total collision rate was calculated, then for the sake of comparison, a fraction of this was taken, corresponding to the fraction of combination divided by total termination. In each case the value of k_d/k_c used by the original authors was employed.

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980. *The Reactions of Alkyl Radicals. Part VIII.* Isobutyl Radicals from the Photolysis of Isovaleraldehyde.*

By Eileen L. Metcalfe and A. F. Trotman-Dickenson.

The photo-initiated chain decomposition of isovaleraldehyde has been studied, and a mechanism accounting for the rates of formation of the principal products constructed. On the assumption that the rate constant for the combination of isobutyl radicals is given by $\log k$ (mole^{-1} cm.^{3} sec.$^{-1}$) = 14, the following Arrhenius parameters of the principal rate-determining reactions have been found (A in mole^{-1} cm.^{3} sec.$^{-1}$ or sec.$^{-1}$; E in kcal. mole^{-1}):

	$\log A$	E
$2C_4H_9 = C_4H_8 + C_4H_{10}$	13·21	0
$C_4H_9 + C_4H_9{\cdot}CHO = C_4H_{10} + C_4H_9{\cdot}CO$	11·7	6·5
$C_4H_9 + C_4H_9{\cdot}CHO = C_4H_{10} + C_4H_8{\cdot}CHO$	12·7	12·6
$C_4H_9 = CH_3 + C_3H_6$	12·8	26·2
$C_4H_9 = H + C_4H_8$	13·0	30·7

The behaviour of isobutyl is compared with that of other alkyl radicals.

Earlier papers in this series recorded the reactions of ethyl,[4] n-propyl,[1] isopropyl,[2] n-butyl,[3] and t-butyl [5] radicals produced in the photo-initiated chain decomposition of the appropriate aldehydes. This paper records a parallel study of isobutyl radicals from isovaleraldehyde. The photolysis of this aldehyde has not previously been fully studied over a range of temperatures, although the rates of the combination, disproportionation, and abstraction reactions of isobutyl radicals produced by the photolysis of di-isobutyl ketone have been measured.[6]

Experimental.—The apparatus and procedure were substantially the same as those previously employed,[1] except that a quartz lens was used to focus the light, and in some runs the intensity of illumination was increased by the introduction of a concave cylindrical aluminium reflector behind the lamp. The condensable fraction of the products was analysed on a column (135 × 0·5 cm.) packed with 3% dinonyl phthalate/60—90 mesh activated alumina, which was heated during the analysis and rose from 20° to 140° in 70 min. From run 42 onwards the carbon monoxide was oxidised with iodine pentoxide (145°) in place of copper oxide (260°). Isovaleraldehyde (L. Light and Co.) was shown to be pure by gas chromatography.

Results and Discussion

Table 1 records the conditions, products, and rate constants derived from the runs. These results show that all the reactions listed below occur during the photolysis. Deductions can be made about the rate constants of the reactions designated by a simple number.

The Photolytic Act, (a), (b), (c), *and* (d).—The primary process in the photolysis of isovaleraldehyde has not been fully investigated though Bamford and Norrish [6] showed that both (*a*) and (*b*) occurred. The present work does not give quantitative data about the processes, but the results show that they all occur. At low temperatures the rate of production of isobutane is roughly constant; it is presumably produced by (*b*). The rate of production of propene, when corrected to unit aldehyde concentration and unit light

* Part VII, Birrell and Trotman-Dickenson, *J.*, 1960, 4218.

intensity, is roughly constant from 26° to 206°; it is produced by (*c*), or possibly by (*d*). The runs below 70° show that (*c*) or (*d*) accounts for about 60% of the decomposition of the aldehyde. Kraus and Calvert [7] state that this type of primary process will occur in any aldehyde or ketone with a straight side-chain of three or more carbon atoms, and also that it will increase in importance as the number of γ-hydrogen atoms increases, because a γ-hydrogen atom is transferred to the α-carbon atom as the bond between the α- and the β-carbon atom breaks. Process (*c*) occurs in the photolyses of n-butyraldehyde,[1] n-valeraldehyde,[3] and 1-methylbutyraldehyde [8] and is most important for isovaleraldehyde which has six γ-hydrogen atoms. Process (*d*) is postulated as well as (*c*) because there is a small constant rate of methane production at low temperatures. It is unlikely that all the methane is a secondary product from, say, the photolysis of acetaldehyde.

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CHO + h\nu \begin{cases} \longrightarrow (CH_3)_2CH{\cdot}CH_2 + CHO & (a) \\ \longrightarrow (CH_3)_3CH + CO & (b) \\ \longrightarrow C_3H_6 + CH_3{\cdot}CHO & (c) \\ \longrightarrow C_3H_6 + CH_3 + CHO & (d) \end{cases}$$

$$2C_4H_9 \xrightarrow{k_1} C_8H_{18} \quad (1)$$

$$2C_4H_9 \xrightarrow{k_2} C_4H_{10} + C_4H_8 \quad (2)$$

$$C_4H_9 + C_4H_9{\cdot}CHO \xrightarrow{k_3} C_4H_{10} + C_4H_9{\cdot}CO \quad (3)$$

$$C_4H_9{\cdot}CO \longrightarrow C_4H_9 + CO \quad (3a)$$

$$C_4H_9 + C_4H_9{\cdot}CHO \xrightarrow{k_4} C_4H_{10} + C_4H_8{\cdot}CHO \quad (4)$$

$$C_4H_8{\cdot}CHO \longrightarrow C_4H_8 + CHO \quad (4a)$$

$$CHO + C_4H_9{\cdot}CHO \longrightarrow H_2CO + C_4H_9{\cdot}CO \quad (4b)$$

$$CHO \longrightarrow H + CO \quad (4c)$$

$$H + C_4H_9{\cdot}CHO \longrightarrow H_2 + C_4H_9{\cdot}CO \quad (4d)$$

$$C_4H_9 \xrightarrow{k_5} CH_3 + C_3H_6 \quad (5)$$

$$CH_3 + C_4H_9{\cdot}CHO \longrightarrow CH_4 + C_4H_9{\cdot}CO \quad (5a)$$

$$2CH_3 \longrightarrow C_2H_6 \quad (5b)$$

$$C_4H_9 \xrightarrow{k_6} H + C_4H_8 \quad (6)$$

Combination of Isobutyl Radicals (1).—This reaction is the source of 2,5-dimethylhexane in the products, which is formed according to the equation $R_{C_8H_{18}} = k_1[C_4H_9]^2$. This rate constant has never been measured; for the purpose of the description of the experimental results, it has been assumed that $k_1 = 10^{14}$ mole^{-1} cm.^{3} sec.$^{-1}$.

Disproportionation of Isobutyl Radicals (2).—Twelve runs that provide direct information on k_2 were carried out between 26° and 124° with concentrations of aldehyde between 1 and 2×10^{-6} mole cm.$^{-3}$. Direct comparison of the rates of formation of isobutene and the octane gave the disproportionation-combination ratio: $k_2/k_1 = R_{C_4H_8}/R_{C_8H_{18}}$. The logarithms of this ratio are plotted against the reciprocal of the absolute temperature in the Figure. The results, calculated by the least-squares method, give $E_2 - E_1 = 0$ and $A_2 = 0{\cdot}165A_1$. Therefore log k_2 (mole^{-1} cm.^{3} sec.$^{-1}$) = 13·21 ± 0·03.

The value of 0·165 does not agree with that of 0·42 found by Kraus and Calvert [7] from the photolysis of di-isobutyl ketone. Their value is probably too high because isobutene can be produced both by disproportionation and by the decomposition of the radical formed when isobutyl abstracts hydrogen from its parent ketone.

If $k_2/k_1 = 0{\cdot}42$, then their results yield by least squares

$$\log k_7 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}) = (11{\cdot}40 \pm 0{\cdot}20) - (7560 \pm 360)/2{\cdot}3RT$$

TABLE 1.

No.	Temp.	Time (sec.)	[Ald.]	CO	H_2	CH_4	C_3H_6	C_4H_{10}	C_4H_8	C_8H_{18}	k_2/k_1	$k_3/k_1^{\frac{1}{2}}$	$k_4/k_1^{\frac{1}{2}}$	$k_5/k_1^{\frac{1}{2}}$	$k_6/k_1^{\frac{1}{2}}$
21R	25·7°	12,000	1·14	18·4	2·69	3·80	12·6	5·18	0·129	0·920	0·140	—	—	—	—
19R	47·0	9600	1·46	21·4	3·30	3·99	29·7	17·1	0·382	2·26	0·169	—	—	—	—
20R	47·8	8400	1·74	30·4	2·39	2·33	37·7	21·9	0·504	2·84	0·178	—	—	—	—
18	66·8	10,800	2·02	21·1	2·30	4·64	27·3	22·8	0·319	2·15	0·149	—	—	—	—
16	86·9	10,800	0·972	10·6	0·829	2·15	11·8	9·89	0·136	0·709	0·192	—	—	—	—
17	90·6	8100	1·22	14·2	0·858	3·22	25·6	18·0	0·195	1·26	0·155	—	—	—	—
15	92·9	11,533	1·25	11·6	1·02	2·93	14·1	16·7	0·200	1·21	0·165	—	—	—	—
4	117·0	9600	1·57	14·8	0·788	4·96	18·5	26·7	0·227	1·77	0·128	12·7	—	—	—
5	117·9	7200	1·77	21·0	0·926	0·918	a.f.	a.f.	0·243	1·43	0·170	—	—	—	—
3	118·2	7041	1·47	20·8	0·963	2·63	22·9	33·7	0·233	1·46	0·159	18·8	—	—	—
1	121·1	10,218	1·48	21·4	1·16	10·7	13·9	20·4	0·227	1·08	0·210	13·1	—	—	—
2	123·9	11,455	1·23	12·6	1·11	17·3	13·2	20·4	0·261	1·57	0·166	13·0	—	—	—
14	141·3	7300	1·57	15·0	0·672	2·89	9·67	26·6	0·225	0·727	—	19·7	—	—	—
13	151·6	4800	1·87	22·8	0·985	2·50	15·6	39·9	0·188	0·777	—	24·1	—	—	—
34	158·5	1800	1·59	41·8	3·11	4·74	29·0	66·2	0·439	1·85	—	30·4	—	—	—
22R	161·2	1200	2·77	110	7·61	25·5	71·8	198	1·16	7·27	—	26·4	—	—	—
23R	165·7	4200	0·675	18·0	2·96	2·96	19·5	26·4	0·323	1·76	—	29·1	—	—	—
33	175·6	1800	1·74	69·6	4·08	4·08	27·0	82·2	0·690	2·07	—	32·7	—	—	—
8	178·4	3664	1·35	31·2	3·22	3·38	12·3	51·6	0·632	0·910	—	39·5	0·374	—	—
7	182·6	3600	1·47	45·6	2·83	1·82	18·8	70·3	0·816	1·412	—	39·8	0·334	—	—
6	184·4	3707	1·27	38·2	2·20	1·92	12·2	57·9	0·731	1·37	—	38·5	0·340	—	—
35	190·1	1500	1·34	58·5	4·04	6·57	20·7	70·0	0·753	1·62	—	40·6	0·285	—	—
37R	191·7	1800	1·06	59·7	5·19	3·64	26·2	83·1	1·16	2·55	—	49·0	0·435	—	—
31	200·1	2400	1·43	93·3	10·3	7·58	30·6	116	1·34	2·12	—	55·2	0·479	—	—
32	205·7	1800	1·73	95·5	9·54	13·9	31·4	150	1·66	1·79	—	64·1	0·647	—	—
12	226·2	2700	1·12	29·6	4·23	8·26	9·10	52·1	0·858	0·377	—	74·8	1·16	—	—
11	230·3	2444	0·938	25·0	2·47	9·47	8·67	49·9	0·855	0·485	—	75·1	1·19	—	—
10	253·9	1201	1·12	93·2	5·13	8·60	24·7	106	2·68	1·22	—	83·1	2·00	—	—
9	258·4	1200	1·21	86·2	5·32	18·7	33·0	135	3·06	0·753	—	126	2·81	—	—
40	278·9	900	1·19	187	11·6	38·5	68·4	261	6·91	2·34 *	—	—	3·61	27·6	—
38	306·1	720	0·957	123	12·4	154	112	224	10·2	1·42 *	—	—	8·74	83·0	—
39	307·5	900	1·17	182	35·7	182	132	291	12·4	1·59 *	—	—	8·24	90·4	—
43	329·0	420	0·954	297	27·2	270	262	291	21·7	1·60 *	—	—	—	196	8·08
42	344·7	480	0·659	294	29·5	292	324	198	21·8	1·18 *	—	—	—	292	11·9
44	373·3	360	0·983	379	62·7	699	681	257	44·6	0·547 *	—	—	—	914	40·8
45	401·4	240	1·03	895	218	920	1153	250	70·4	0·304 *	—	—	—	2085	97·5
46	417·6	120	1·14	858	135	2328	2057	341	138	0·361 *	—	—	—	3418	187

Rates of formation of products are given as 10^{-12} mole cm.$^{-3}$ sec.$^{-1}$. [Ald.] is the mean concentration of aldehyde, in 10^{-6} mole cm.$^{-3}$. $k_3/k_1^{\frac{1}{2}}$ and $k_4/k_1^{\frac{1}{2}}$ are in mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$; $k_5/k_1^{\frac{1}{2}}$ and $k_6/k_1^{\frac{1}{2}}$ are in 10^6 mole$^{-\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-\frac{1}{2}}$.

* Calculated value. a.f. = analytical failure. R = reflector present.

for the abstraction reaction (7). If the value of $k_2/k_1 = 0{\cdot}165$ found in this work is used in

$$C_4H_9 + C_4H_9{\cdot}CO{\cdot}C_4H_9 \xrightarrow{k_7} C_4H_{10} + C_4H_9{\cdot}CO{\cdot}C_4H_8 \quad \ldots\ldots (7)$$

the recalculation of Kraus and Calvert's results, then

$$\log k_7 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}) = (11{\cdot}06 \pm 0{\cdot}09) - (6830 \pm 160)/2{\cdot}3\boldsymbol{R}T$$

Thus the errors are halved by the adoption of the lower value of k_2/k_1. It is impossible to derive an accurate value of k_2/k_1 from Kraus and Calvert's work but their results are compatible with the value obtained here.

Abstraction of Hydrogen Atoms from Isovaleraldehyde (4).—Above 178° the rate of formation of isobutene rose sharply. The temperature is too low for decomposition of the isobutyl radical. The extra isobutene can be accounted for by reaction (4) followed by (4*a*). Hence,

$$\begin{aligned} C_4H_8 \text{ (reaction 4}a\text{)} &= C_4H_8 \text{ (total)} - C_4H_8 \text{ (reaction 2)} \\ &= C_4H_8 \text{ (total)} - 0{\cdot}165C_8H_{18} \end{aligned}$$

where the reactions noted in parentheses are those by which the products are formed. Therefore,

$$R_{C_4H_{10}} \text{ (reaction 4)} = R_{C_4H_8} \text{ (reaction 4}a\text{)} = k_4 [C_4H_9][C_4H_9{\cdot}CHO]$$

and

$$k_4/k_1^{\frac{1}{2}} = R_{C_4H_8} \text{ (reaction 4}a\text{)}/R_{C_8H_{18}}^{\frac{1}{2}} [C_4H_9{\cdot}CHO]$$

The values of this ratio between 178° and 307°, plotted in the Figure, and calculated by the least-squares method, yield

$$\log k_4 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}) = (12{\cdot}62 \pm 0{\cdot}05) - (12{,}700 \pm 200)/2{\cdot}3\boldsymbol{R}T$$

The runs at 307° were neglected in this calculation because some isobutene may be produced by reaction (6) at this temperature.

Reactions (4*c*) and (4*d*) are postulated because the rate of hydrogen production increased with that of isobutene. Reaction (4*b*) is suggested because it is known to follow the reaction analgous to (4) in the photolyses of n-butyraldehyde,[1] isobutyraldehyde,[2] and pivalaldehyde,[5] but it is less certain in the case of isovaleraldehyde because the rate of hydrogen production was always greater than that of isobutene. It is probable that the hydrogen atom abstracted in reaction (4) is the tertiary atom, because the radical thereby produced can form isobutene directly.

Abstraction of Hydrogen Atoms from Isovaleraldehyde (3).—According to the mechanism, the rate of attack of isobutyl on the carbonyl hydrogen atom in isovaleraldehyde can be taken as

$$R_{C_4H_{10}} - R_{C_4H_8(2)} - R_{C_4H_8(4a)}$$

Hence $k_3/k_1^{\frac{1}{2}} = R_{C_4H_{10}} - R_{C_4H_8}/R_{C_4H_{18}}^{\frac{1}{2}}[C_4H_9{\cdot}CHO]$.

At the temperatures considered no isobutene was produced by decomposition of isobutyl, so

$$R_{C_4H_8} \text{ (total)} = R_{C_4H_8} (2) + R_{C_4H_8} (4a)$$

$k_3/k_1^{\frac{1}{2}}$ was determined in 19 runs between 117° and 230° at aldehyde concentrations between 0·7 and $3{\cdot}1 \times 10^{-6}$ mole cm.$^{-3}$. The results, plotted in the Figure and calculated by the least squares method, yield

$$\log k_3 \text{ (mole}^{-1} \text{ cm.}^3 \text{ sec.}^{-1}) = (11{\cdot}71 \pm 0{\cdot}07) - (6500 \pm 100)/2{\cdot}3\boldsymbol{R}T$$

The changes in aldehyde concentration and a change in light intensity produced by the use of the reflector in some runs did not affect the rate constants. A series of five consecutive runs in which $\log k_3/k_1^{\frac{1}{2}}$ was uniformly slightly high has been rejected: an impurity

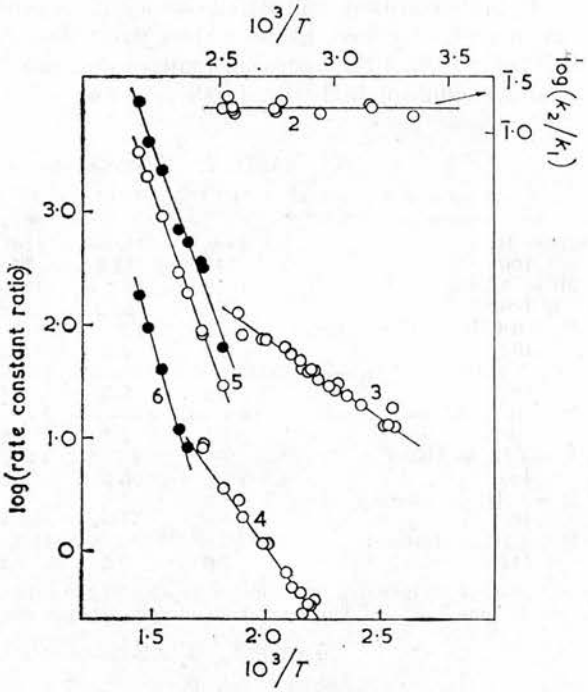
was probably present in the aldehyde, because a fresh sample yielded normal rate constants.

Decomposition of Isobutyl to Propene (5).—Above 279° the rate of formation of propene rose sharply. This was attributed to reaction (5) and hence,

$$k_5/k_1^{\frac{1}{2}} = \{R_{C_3H_6}\text{ (total)} - R_{C_3H_6}\text{ (initial act)}\}/R_{C_5H_{12}}^{\frac{1}{2}}$$

For 25 runs below 206° the rate of propene production, corrected to unit aldehyde concentration and unit light intensity, varied between 11·4 and 34·4 $\times$ 10^{12} moles cm.$^{-3}$ sec.$^{-1}$. On average $R_{C_3H_6}$ (initial act)/$[C_4H_9{\cdot}CHO]R_{C_5H_{12}} = 9{\cdot}5$.

This correction was applied in the calculation of k_5. At the lowest temperature at which k_5 was determined the propene from the initial act was 40% of the total, but at the highest temperature it contributed less than 1% to the total propylene.



Arrhenius plots for the reactions of isobutyl: (2) *disproportionation*, k_2/k_1; (3) *hydrogen abstraction*, $k_3/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$); (4) *hydrogen abstraction from alkyl group*, $k_4/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$); (5) *decomposition to methyl and propylene*, $10^6k_5/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$)—*open circles, results based on propene; filled circles and line, results based on methane* (*which are displaced upwards by* 0·4 *log unit*); (6) *decomposition to hydrogen and isobutene*, $10^6k_6/k_1^{\frac{1}{2}}$ (*mole*$^{-\frac{1}{2}}$ *cm.*$^{-\frac{3}{2}}$ *sec.*$^{-\frac{1}{2}}$).

At these temperatures the runs were short and the amount of octane produced was too small to be measured; it was therefore calculated from $R_{C_4H_{10}}$, k_1, k_3, and k_4. Eight runs between 279° and 417° are plotted in the Figure, and the results, calculated by the least-squares method, give

$$\log k_5\text{ (sec.}^{-1}) = (12{\cdot}82 \pm 0{\cdot}08) - (26{,}200 \pm 300)/2{\cdot}3\boldsymbol{R}T$$

Similarly, from the mechanism,

$$k_5/k_1^{\frac{1}{2}} = (R_{CH_4} + 2R_{C_2H_6})/R_{C_5H_{12}}^{\frac{1}{2}}$$

Even at the highest temperatures the amount of ethane produced was very small, and was neglected. The results, calculated by least squares from the rate of methane production, give

$$\log k_5\text{ (sec.}^{-1}) = (12{\cdot}36 \pm 0{\cdot}31) - (24{,}700 \pm 1100)/2{\cdot}3\boldsymbol{R}T$$

The results calculated on methane show less precision than those calculated on propene, but they almost agree within experimental error.

Decomposition of Isobutyl to Isobutene (6).—Above 329° the rate of formation of isobutene rose sharply and could no longer be accounted for by reactions (4) and (4*a*). This was attributed to reaction (6), and hence

$$k_6/k_1^{\frac{1}{2}} = \{R_{C_4H_8} - R_{C_4H_8}\text{ (reaction 4}a\text{)} - R_{C_4H_8}\text{ (reaction 2)}\}/R_{C_8H_{18}}{}^{\frac{1}{2}}$$

or $k_6/k_1^{\frac{1}{2}} = R_{H_2}/R_{C_8H_{18}}{}^{\frac{1}{2}}$.

The rate of octane formation was again calculated from $R_{C_4H_{10}}$, k_1, k_3, and k_4. The isobutene from reaction (4*a*) was calculated; that from reaction (2) was negligible. Five runs between 329° and 417° at aldehyde concentrations of about $0{\cdot}9 \times 10^{-6}$ mole cm.$^{-3}$ are shown in the Figure, and yield

$$\log k_6\ (\text{sec.}^{-1}) = 13{\cdot}0 - (30{,}700/2{\cdot}3\boldsymbol{R}T)$$

The rate constants calculated on the rate of production of hydrogen were very scattered but in each case gave higher values than those calculated on the isobutene production. It is believed that the hydrogen analyses were unreliable, because it is difficult to determine small amounts of hydrogen in the presence of large amounts of carbon monoxide and methane.

TABLE 2. *The reactions of alkyl radicals.*

Radical R Reaction	Et [4]	Pr^n [1]	Pr^i [2]	Bu^n [3]	Bu^s [8]	Bu^i	Bu^t [5]
$2R = R_2$	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*	14·0, *0*
100°	**14·0**	**14·0**	**14·0**	**14·0**	**14·0**	**14·0**	**14·0**
2R = Alkane + Alkene	13·2, *0*	13·2, *0*	13·8, *0*	14·6, *1·3*	14·3, *0*	13·2, *0*	14·6, *0*
100°	**13·2**	**13·2**	**13·8**	**13·9**	**14·3**	**13·2**	**14·6**
R + R·CHO = RH + R·CO	11·1, *5·9*	11·3, *6·7*	11·3, *6·3*	10·9, *5·4*	10·7, *4·9*	11·7, *6·5*	10·5, *4·3*
182°	**8·3**	**8·3**	**8·3**	**8·3**	**8·3**	**8·6**	**8·4**
CH_3 + R·CHO = CH_4 + R·CO	12·0, *7·5*	11·8, *7·3*	12·6, *8·7*	12·1, *8·0*	13·1, *10·4*	12·3, *8·4*	13·0, *10·2*
182°	**8·2**	**8·3**	**8·4**	**8·2**	**8·2**	**8·2**	**8·2**
R = H + Alkene	14·0, *40* [10]	13·6, *35*	13·8, *37*	—	—	13·0, *31*	16·3, *44*
400°	**1·1**	**2·2**	**1·8**	—	—	**3·0**	**2·2**
R = CH_3 + Alkene	—	11·7, *25*	12·0, *33*	12·1, *27*	11·7, *24*	12·8, *26*	16·0, *46*
400°	—	**3·5**	**1·0**	**3·3**	**3·9**	**4·3**	**1·0**
R = C_2H_5 + Alkene	—	—	—	11·2, *22*	—	—	—
400°	—	—	—	**4·1**	—	—	—
R + C_2H_4 = Radical	12·1, *8·6*	10·9, *6·5*	11·4, *6·9*	11·1, *7·3*	—	—	11·2, *7·1*
142°	**7·6**	**7·5**	**7·8**	**7·3**	—	—	**7·5**

The A factors (log, in ordinary type) and the rate constants (log, in bold type) are in sec.$^{-1}$ and mole^{-1} cm.^{3} sec.$^{-1}$. The activation energies (italics) are in kcal. mole^{-1}.

TABLE 3. *The decomposition of alkyl radicals.*

	Et [4]	Pr^n [1]	Pr^i [2]	Bu^n [3]	Bu^s [8]	Bu^i	Bu^t [5]
Loss of hydrogen							
ΔH	39	37	41	—	—	35	42
E	40 [9]	35	37	—	—	31	44
Loss of methyl							
ΔH	—	25	(29)	(22)	26	25	(32)
E	—	25	33	27	24	26	46
Loss of ethyl							
ΔH	—	—	—	23	—	—	—
E	—	—	—	22	—	—	—

ΔH and E are in kcal. mole^{-1}.

ΔH based on D(Me–H) = 102·5, D(primary–H) = 97, D(secondary–H) = 93, D(tertiary–H) = 90. The values of ΔH in parentheses indicate that the reaction involves a rearrangement.

Comparison of Isobutyl with Other Alkyl Radicals.—The value of $E_2 - E_1 = 0$ for the disproportionation reaction is in agreement with previous work on the alkyl radicals, with the exception of n-butyl,[3] which shows a small activation energy for disproportionation (see Table 2).

The Arrhenius parameters for the abstraction reaction (3) agree fairly well with those of other alkyl radicals; also log k_3 at 182° is similar to the other abstraction-rate constants.

The activation energy for the decomposition to methyl and propene is close to the value for the heat of reaction (25 kcal. mole^{-1}) (see Table 3). This is true for all alkyl radicals that decompose to give methyl and an alkene without rearrangement. However, E_5 is certainly low because the activation energy for the addition of methyl to propene has been estimated to be 6 kcal. mole^{-1},[9] in line with activation energies found for other addition reactions.

The activation energy for the decomposition to hydrogen and isobutene is again probably low, because in common with those of the other alkyl radicals that decompose to give hydrogen without rearrangement, it is a few kcal. mole^{-1} less than the heat of reaction (see Table 3).

The A factors for both decompositions should be 10^{13} sec.$^{-1}$, if the entropies of the radicals and the A factors for the addition reactions are assumed to be normal. In both cases the experimental A factors are close to this value.

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